



AGRICULTURAL RESEARCH INSTITUTE
PUSA

Transactions of the Faraday Society

Transactions of the Faraday Society.

FOUNDED 1903

TO PROMOTE THE STUDY OF ELECTROCHEMISTRY, ELECTROMETALLURGY,
PHYSICAL CHEMISTRY, METALLOGRAPHY, AND KINDRED SUBJECTS.

VOL. XXVIII. 1932

GURNEY AND JACKSON
LONDON: 33 PATERNOSTER ROW
EDINBURGH TWEEDDALE COURT

ABERDEEN: THE UNIVERSITY PRESS

STUDIES IN GELS I. SYNERESIS OF SILICA GEL.

BY D. G. R. BONNELL.

Received 7th September, 1931.

Graham¹ in the course of his well-known studies on silicic acid gels, observed that, when a freshly-prepared specimen was allowed to stand before dialysing, it exhibited a very peculiar property, *viz.*, liquid was spontaneously exuded from the gel. This exudation of liquid went on for days, while the gel simultaneously contracted visibly. This phenomenon Graham called "syneresis."

This extraordinary property of silicic acid gels remained unnoticed, until Ostwald² in 1915, again drew the attention of colloid chemists to the phenomenon. He pointed out that syneresis was not, by any means, a property peculiar to silica gels, but that it seemed to be a property pertaining to gels in general. He showed that gels of substances of widely different properties, *e.g.* silica, vanadium pentoxide, dyes, soap, rubber, viscose, etc., all possessed this property of being able to exude liquid after setting. Later investigations have corroborated his statement and shown that all gels exhibit syneresis.

The quantitative study of this property has been very much neglected and consequently the literature on the subject is scanty. The following is an account of a systematic study of this phenomenon—as applied to silica gel—which was undertaken as part of an investigation of the properties of gels.

Experimental.

The materials used for the preparation of the various gels investigated gave the following analyses:—

Sodium Silicate.

$\text{Na}_2\text{O} = 9.5$ per cent. $\text{SiO}_2 = 30.5$ per cent., and traces of iron, corresponding to a molar ratio, $\text{Na}_2\text{O} : \text{SiO}_2 = 1 : 3.3$.

The samples of sulphuric, hydrochloric, and acetic acids employed were pure analytical reagents.

Volume Changes on Syneresis.

Ferguson and Appleby³ found, with gels of p_H 5.0 and silica concentration 7 per cent., that no total volume change accompanied syneresis, *i.e.*, the sum of the volumes of the gel and exuded liquid remained constant. Since gels of varying p_H were to be used during this investigation, it was necessary to test whether the same volume relations applied to strongly alkaline gels. For this purpose a simple apparatus was devised.

¹ Graham, *Phil. Trans.*, 151, 205, 1861; *J. Chem. Soc.*, 17, 318, 1864.

² Ostwald, *Die Welt der vernachlässigten Dimensionen*, 1 Auflage, 76.

³ Ferguson and Appleby, Rept. of Building Research Board, 1928, 53; *Trans. Faraday Soc.*, 26, 642, 1930.

It consists essentially of a flask with a manometer attached, as shown in Fig. 1. The inside of the flask F was covered with a thin film of vaseline

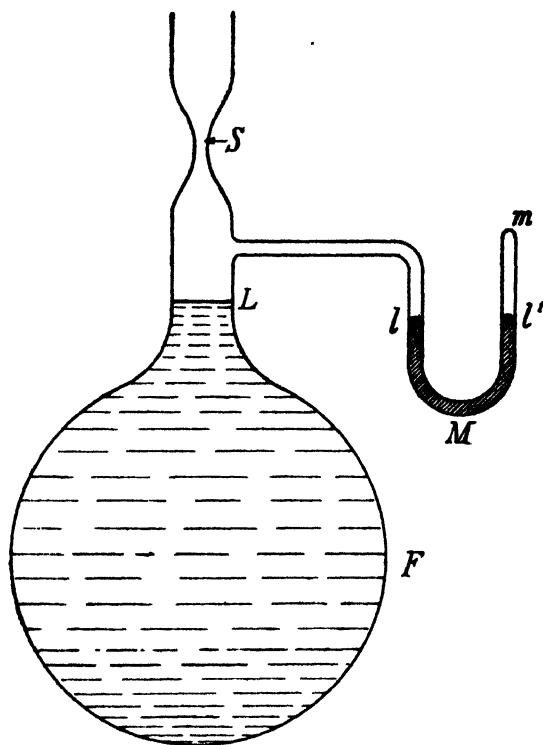


FIG. 1.

to avoid adhesion of the gel to the sides. The neck was drawn out into a fine constriction, through which the flask was filled with the sol—up to the mark L. The flask and contents were sealed off at the constriction S. The manometer M was so arranged that after sealing, the mercury menisci in the two arms were at the same level. The volumes LSl and $l'm$ could be calculated from the diameters of the tubes and the volume of the sol was known. The ratio of these volumes was such that a variation of 1 in 1600 in the volume of the gel was represented by 1 mm. difference in level of the mercury in the manometer. During the experiment the whole apparatus was immersed in a constant temperature bath.

Solutions of p_H 11.0 and silica concentration 9.7 per cent. were used. At the end of ten days the liquid synerised amounted to roughly 90 per cent. of the volume of the original gel, but no change was observed in the manometer mercury levels. From this it is concluded that no volume change accompanies syneresis whether the gels are alkaline or acidic.

Determination of Velocity of Syneresis.

Up to the present, most of the methods which have been employed for the determination of the velocity of syneresis and for the estimation of the total quantity of syneretic liquid given off by any particular gel, are not capable of yielding very accurate results.

Some of the first investigators in this field were Holmes, Kaufmann, and Nicholas,⁴ who studied the relation between the quantity of liquid synerised and vibrations produced by small impacts. Silica gels were prepared in vaselined tubes, and the amount of liquid exuded by the gel measured. The method employed for this purpose is not described.

Pijper and Kraan⁵ determined the volume of syneretic liquid given off by Agar gels as follows:—

⁴ *J. Am. Chem. Soc.*, **41**, 1329, 1919.

⁵ *Med. Journ. of South Africa*, **16**, 221, 1921.

Cylinders of agar gels were placed in a slightly larger cylinder, and the liquid exuded was allowed to drop from the gel into a measuring tube. The whole system was kept at a constant temperature.

Liepatoff,^{6, 7} has carried out a series of investigations on the syneresis of geranin gels. In the earlier work he prepared the gels either in a separating funnel or in a conical flask, wherein it was allowed to synerise for twenty hours. At the end of this period the liquid phase was removed and measured. He later⁷ modified this method by preparing the gels in glass cylinders, and after syneresis was considered to have reached its maximum value, the contents were poured on to a perforated filter funnel and the volume of the filtrate determined. This was taken as the total volume that would be exuded by the gel.

Mukoyama⁸ investigated the syneresis of viscose gels by placing 20 c.c. of the viscose sol in a test-tube, which was then sealed and placed in a constant temperature bath at 17° C. The sol set and, after syneresis had become visible, the liquid exuded was measured by breaking the seal and pouring the synereticum into a measuring cylinder. After determining the volume, the liquid was again poured back into the original tube, which was resealed and replaced in the bath. This operation was repeated at definite time intervals. A correction was introduced for the small losses due to evaporation and measurements.

Obviously all the above methods do not admit of any accurate quantitative measurements of the syneresis of gels. A more satisfactory method was devised by Ferguson and Appleby.³ An apparatus was constructed wherein the gel floated on the surface of a layer of carbon tetrachloride. At any period after syneresis had commenced, the volume of liquid phase was determined by forcing the carbon tetrachloride past the gel into a graduated tube. During this operation, the heavy organic liquid displaced the syneretic liquid present and carried it into the measuring tube, where its volume could be determined. After measurement the tetrachloride was withdrawn into its original position, thereby bringing the syneretic liquid back into contact with the gel. The whole apparatus was a closed system thereby eliminating losses due to evaporation.

Although very consistent readings are possible with this method, an alternative method was sought to eliminate the use of an inert liquid coming into contact with the gel. With this in view the apparatus described below was devised and used in the succeeding investigations.

The apparatus is shown diagrammatically in Fig. 2. It consists of two main parts, A and B. A is a glass tube, 4 cm. wide, joined at its

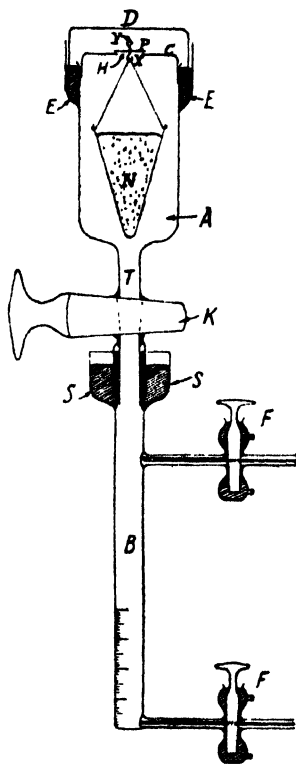


FIG. 2.

⁶ *Koll. Z.*, 41, 200, 1927.

⁷ *Ibid.*, 43, 396, 1927.

⁸ *Ibid.*, 42, 79, 1927.

lower extremity, through a narrower tube T (of 1 cm. diameter), to a glass stopcock K, whose bore tapers as shown. The upper extremity of A is closed by a ground glass cap C, which is provided with a centrally placed hole H (0.5 cm. diameter). Resting over this hole is a metal plate P, to which are attached suspension hooks X and Y. When P is in position, as in the diagram, one hook, X, protrudes a little way into the chamber A. A specially-prepared filter cone N, can be suspended from X by means of a fine nickel wire. This filter cone is made of similar material to the ordinary Soxhlet extractor, and is of such dimensions that it can be freely suspended inside A.

The cap C and plate P are protected by another cap D, which, in conjunction with the mercury seal E, serves to close the system.

B is a glass tube, about 1.2 cm. wide, graduated to 0.1 c.c., fitted at its upper and lower ends with two capillary side tubes with mercury sealed stopcocks F.

A and B are connected by means of the ground joint shown. Owing to the fact that, during an experiment, the whole apparatus is completely immersed in water, it was found desirable to protect the joint by the mercury seal S.

To obviate the possibility of retardation of the syneretic process by the adhesion of the gel to the sides of the filter cone, the following method was adopted :—

A cone, identical in shape and size with the filter cones used in the experiments, was coated with a thin layer of vaseline to prevent adhesion. This particular cone could be opened and, by inverting on a glass plate, could be easily removed from any contained gel. The solutions for preparing the gel were mixed and poured into this cone, and there allowed to set. Immediately this took place, the gel was removed and placed in the experimental cone, which had previously been saturated with the syneretic liquid of a similar gel and weighed.

The whole operation of removing the gel and transferring from one cone to the other need not take more than ten to fifteen seconds.

The cone and gel were now placed in position in section A of the apparatus, which, by means of a special stand, could be brought under the beam of a balance. By attaching the hook Y to the beam, the cone and contents were weighed. The two parts A and B were then joined, placed in another stand, and the whole completely immersed in a constant temperature bath.

The apparatus was taken from the bath periodically, section A removed, and the gel weighed. By this means the loss in weight of the gel could be determined. The time taken over this operation was small, as an approximate value of the loss in weight was known from the volume of liquid in B. This means that errors in the results due to temperature effects are negligible.

The cone, having been previously saturated with the syneretic liquid, would not retain any liquid exuded by the gel, with the result that the syneretic liquid filtered through as it was formed. The loss in weight of the cone and contents, therefore, gave a quantitative measure of the syneresis of the gel. Any loss due to evaporation was excluded as the system was a closed one. As syneresis proceeded the gel shrank within the conical container, but always remained in contact with the walls and therefore with its syneretic liquid.

As the cone was suspended centrally in A the liquid exuded dropped directly into the graduated tube of B. This permitted, when necessary,

the determination of the volume synerised at any given time, within the accuracy of the graduations.

By means of the stopcocks F, small quantities of liquid could be extracted for analysis, so that its composition could be determined at any period.

The velocity of syneresis under various pressures may also be investigated with this apparatus. The perforated cap C is replaced by a well-ground stopper, from which the cone and contents may be suspended. This makes the apparatus perfectly airtight without the use of the mercury seals. The upper stopcock F can be attached to a manometer and the lower to a vacuum pump, so that any desired pressure below atmospheric is attainable.

Effect of Adhesion Forces on Syneresis.

Holmes, Kaufmann and Nicholas ⁴ found that gels formed in vaselined tubes synerised and contracted much more than those prepared in clean glass tubes. They observed that in the latter case the gels adhered to the glass walls, while in the former they were able to contract unimpeded.

In order to measure the effect of these adhesive forces on the progress of syneresis, two experiments were carried out: (a) the gel was prepared as described above, (b) the sol was allowed to set in the same filter cone as was used during the syneresis experiment.

The results are given in Table I.

TABLE I.

Setting Time of Gel = 3 minutes. Silica Concentration = 6.5 per cent. Gel (a).		$p_H = 5.0$. Temperature, 30° C. Gel (b).	
Time in hrs. after Setting.	Wt. of Liquid in grms. Synerised per 100 grms. gel.	Time in hrs. after Setting.	Wt. of Liquid in grms. Synerised per 100 grms. gel.
1.0	7.151	1.5	4.385
3.0	10.940	2.5	5.370
19.5	16.008	6.0	6.420
43.5	16.548	19.0	8.890
91.5	17.422	30.0	11.615
139.5	17.838	52.5	12.225
		76.0	12.470
		101.0	12.520
		172.0	13.048

Inspection of the gel (b) at the end of the experiment showed that it had not undergone uniform contraction, and had adhered firmly to one side of the filter cone. On the other hand, gel (a) was free from the cone and had contracted quite uniformly.

Fig. 3 shows the results graphically. It is obvious from the curves that the adhesion of the gel to the filter cone may have a very marked effect upon both the velocity of syneresis, and the final volume of liquid exuded—the latter being decreased in the samples examined by about 25 per cent. The inhibitory effect of such adhesive forces must, therefore, be carefully avoided during any measurement of the quantity of liquid exuded by a gel.

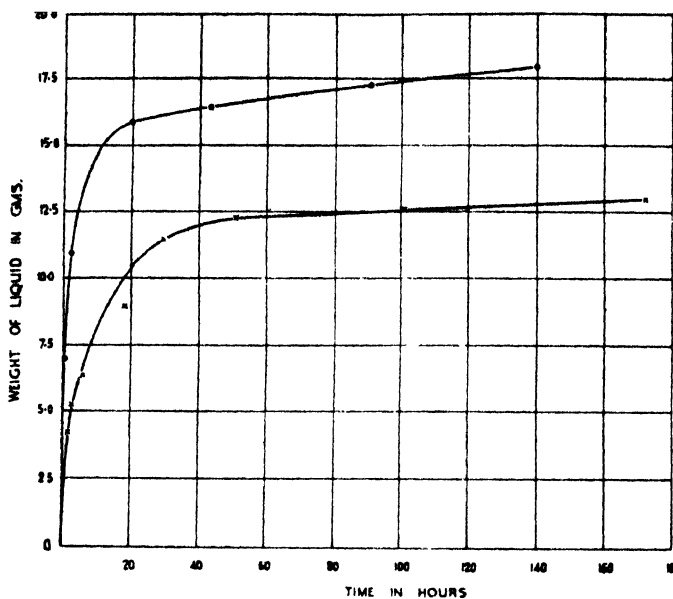


FIG 3

Effect of Silica Concentration on Syneresis.

The first observations on the effect of silica concentration on syneresis were made by Holmes, Kaufmann and Nicholas.⁴ They found that the quantity of syneretic liquid exuded by silicic acid gels increased with increasing concentration.

Similar conclusions were reached by Mukoyama⁸ and Liepatoff⁹ regarding viscose gels of constant alkali content, and Ferguson and Appleby³ concerning silicic acid gels.

On the other hand, Liepatoff¹⁰ found that the reverse was true regarding geranin gels. The velocity of syneresis with these gels increased with increasing concentration, but the total volume of liquid exuded was greater for the more dilute gels. Similar results were obtained by Pijper and Kraan⁵ with agar gels and by Meyer¹¹ with arrowroot.

In preparation of sols of varying silica concentration, great care must be exercised in order that the electrolyte and the hydrogen ion concentrations of the resultant sols may be identical. To ensure this, the procedure adopted by Ferguson and Appleby³ was utilised. This consists in diluting the more concentrated sol with the syneretic liquid of a gel of identical composition. In this way, since the syneretic liquid is of the same p_H as the initial gel, and its electrolyte concentration is in equilibrium with that of the gel, a whole series of gels differing only in silica concentration can be prepared.

To prepare the initial gel accurately measured quantities of sodium silicate of 1.2 density and 1.75 N acid were intimately mixed and treated as described above. The p_H of the gels was kept at a constant value of

⁹ Liepatoff, *Koll. Z.*, **49**, 441, 1929.

¹⁰ *Koll. Z.*, **47**, 21, 1929, see also *Koll. Z.*, **41**, 205, 1927; **43**, 396, 1927.

¹¹ *Koll. Chem. Beih.*, **5**, 1, 1913.

TABLE II.

Gel Concentration SiO ₂ per cent.	Induction Period. (secs.).	Setting Time. (secs.).	Time in hrs. after Setting.	Wt. of Liquid in grms. Synerised per 100 grms. gel.
<i>Gels prepared with Sulphuric Acid. p_H of gels = 8.0.</i>				
8.8	5	3	1.0	13.174
			3.0	16.202
			5.25	16.932
			29.0	18.410
			47.0	18.579
			70.0	18.748
7.04	42	6	1.0	10.160
			3.5	14.672
			20.0	17.212
			44.0	17.608
			72.0	18.422
			164.0	18.700
5.0	60	12	1.5	9.397
			3.75	10.988
			20.25	13.540
			68.25	13.756
			140.25	14.505
4.5	68	15	1.5	6.854
			4.0	8.876
			7.0	10.072
			23.6	12.698
			49.0	14.075
3.0	90	40	81.5	14.900
			1.0	9.866
			3.0	16.110
			21.25	25.071
			44.75	28.551
			98.75	32.173

Gels prepared with Hydrochloric Acid. p_H of gels = 8.0.

8.8	60	4	1.0	12.485
			2.0	14.881
			6.5	16.356
			30.5	17.924
			48.3	18.257
			72.3	18.390
7.04	70	6	1.0	9.525
			3.0	12.860
			23.0	15.310
			75.0	15.990
6.2	76	7	170.0	16.250
			1.5	10.785
			3.5	12.610
			20.0	15.045
4.0	100	15	68.0	15.375
			188.0	16.073
			1.0	8.086
			6.0	13.397
2.6	120	30	33.0	16.555
			47.5	16.940
			100.5	17.800
			1.0	11.531
			3.0	18.411
			21.25	30.794
			44.75	34.060
			98.75	36.496

SYNERESIS OF SILICA GEL

TABLE II. (continued).

Gel Concentration SiO ₂ per cent.	Induction Period. (secs.).	Setting Time. (secs.).	Time in hrs. after Setting.	Wt. of Liquid in grms. Synerised per 100 grms. gel.
<i>Gels prepared with Acetic Acid. p_H of gels = 8.0.</i>				
8.8	5	3	1'75	9'234
			19'5	11'915
			43'5	12'440
			74'0	12'688
			143'5	12'688
7.04	80	8	2'0	9'10
			4'3	10'10
			22'5	11'55
			53'0	11'90
			98'0	12'035
5.0	100	10	2'0	2'500
			4'0	3'755
			21'0	7'750
			44'5	8'120
			73'5	8'250
			98'0	8'415
			122'0	8'501
4.0	130	20	1'0	5'760
			3'0	7'653
			48'0	15'070
			53'0	15'306
			77'0	15'551
			101'0	15'743
			125'0	16'084
			149'0	16'268
			221'0	16'670
			269'0	16'898
2.6	160	40	1'5	10'749
			2'5	13'283
			5'0	16'681
			28'0	25'816
			72'0	30'450
			125'0	32'745
			215'0	34'775
<i>Gels with Sulphuric Acid. p_H of gels = 5.0.</i>				
11.0	20	8	2'0	11'459
			4'5	13'303
			23'25	15'640
			75'0	16'694
			95'5	16'892
7.8	60	20	1'5	8'859
			3'0	10'986
			21'66	14'756
			72'5	15'717
			93'66	15'758
4.5	600	720	2'0	7'429
			5'0	12'310
			23'0	19'577
			47'0	22'722
			143'0	26'030

8.0 in some cases, and 5.0 in others, and was determined with the B.D.H. universal indicator. For the more dilute gels, the measured volumes of syneretic liquid necessary, were added to the acid before the addition of the silicate. This was found to be essential with quick setting gels, as it was impossible to add the diluent to the sol itself, and at the same time ensure the homogeneous distribution of the silica concentration throughout the sol, before setting occurred. Three series of gels were prepared, using sulphuric acid, hydrochloric acid and acetic acid, with sodium silicate. The same silicate solution was used throughout a series of experiments, while the temperature was kept constant at 20° C. The results are given in Table II.

Ferguson and Appleby showed that the electrolyte concentration of the syneretic liquid remained constant throughout the period of syneresis. During the above experiments the syneretic liquid was analysed

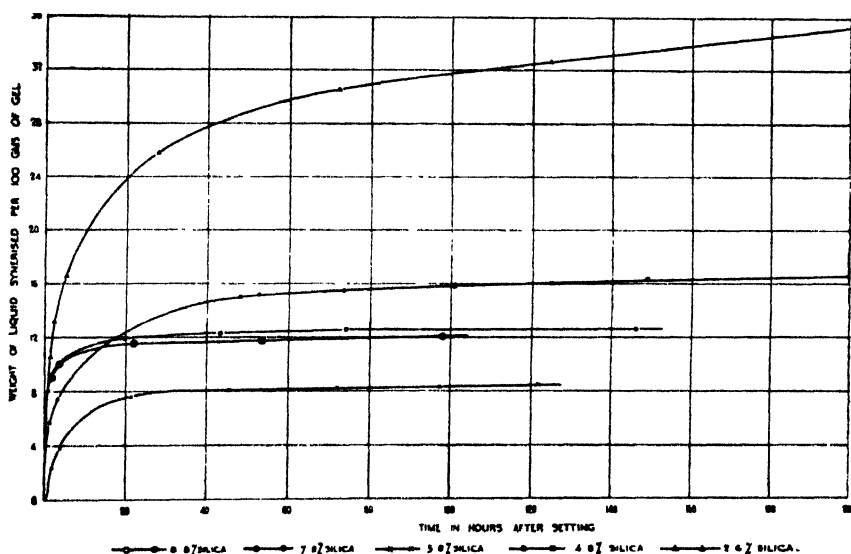


FIG 4

for silica content. The results showed that for the p_H value 8.0, the silica content was constant throughout the experiment at 0.1 per cent. SiO_2 . This was independent of the silica concentration of the gel and was probably dissolved in the molecular state in the syneretic liquid. This low silica concentration of the syneretic liquid is only typical of nearly neutral gels, as will be shown in a later paper on the effect of hydrogen ion concentration on the syneresis of silica gels.

Fig. 4 shows a typical example of the curves obtained in the above results.

Discussion of Results.

In Fig. 5 is shown the effect of the silica concentration of the initial gel on the setting time, and on the induction period elapsing before visible exudation of liquid.

Within certain limits of silica concentration, the initial velocity of syneresis and the final volume of liquid exuded increase, with increasing concentration. In this range the results are in complete agreement with those of Ferguson and Appleby³ and Holmes.⁴ This means, as the former investigators point out, that the greater quantity of liquid is exuded from the gel containing the smaller amount of dispersion medium.

This is, however, not true for very dilute gels. From Fig. 6, which shows the variation of the total quantity of liquid exuded with the initial silica concentration of the gel, it is clear that at concentrations of about 4 per cent. SiO_2 the gel shows a tendency to exude increasing quantities of liquid. The minimum exudation of liquid occurs at roughly the same silica concentration with the three types of gel.

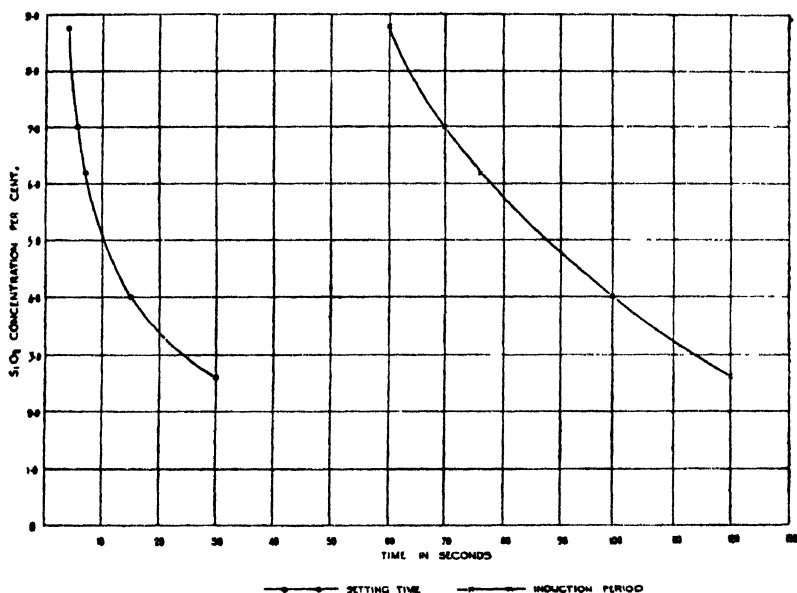


FIG 5

The following is suggested as a tentative explanation for this behaviour:—

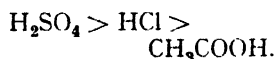
It is very probable that the rigidity of the structure of a fresh gel depends, to a large extent, upon the silica concentration. When, therefore, this concentration is greatly decreased, the structure of the gel formed on setting, becomes too weak to support the weight of the gel, and there will be a tendency for the structure to collapse, setting free some of the retained liquid. This tendency can be observed when such a gel is prepared in a geometrical form and allowed to stand on a glass plate, when it very soon either loses its original form or shows a marked distortion due to slump.

Thus, when these very dilute gels are exposed to such conditions, the liquid exuded is the result of two influences, *viz.*:— the rearrangement possibly due to the attracting forces between the micelles, and the hydrostatic pressure on the gel. The effect of an applied pressure on the process of syneresis is now under investigation.

The Specific Effect of the Coagulant.

From the data given in Tables I.-II. the specific effect of hydrochloric, sulphuric and acetic acids can be obtained for certain silica concentrations.

The results show that for the same p_H and silica concentration the progress of syneresis varies with the acid used for the preparation of the gel. The acid not only influences the velocity of syneresis, but it considerably affects the total volume of liquid given off, *i.e.*, the final equilibrium depends to a great extent upon the coagulant used. The influence exerted by these three acids is in the order



A more detailed study of the effect of the presence of electrolytes is being carried out, and the results will be communicated in a later paper.

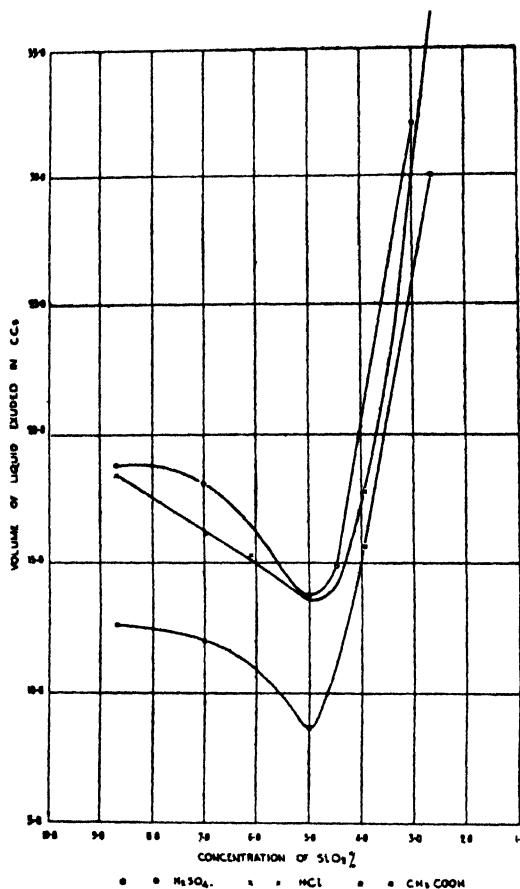


FIG. 6

Summary.

A new type of synerometer has been devised by means of which the velocity of syneresis and the final equilibrium can be quantitatively studied.

By means of this apparatus the influence of the silica concentration of silicic acid gels upon the progress of syneresis has been investigated. For this purpose gels were prepared by means of the action of hydrochloric, sulphuric, and acetic acids on sodium silicate.

The volume changes accompanying syneresis have also been investigated.

The author takes this opportunity of expressing his indebtedness to the Director of the Building Research Station for the untiring interest which he has shown in the investigation, and for kind permission to publish these results. In addition, the author's thanks are due to Mr. B. H. Wilsdon for many helpful criticisms and suggestions.

*Building Research Station,
Bucknall's Lane,
Garston, Herts.*

STUDIES IN GELS II. EFFECT OF HYDROGEN ION CONCENTRATION ON THE SYNERESIS OF SILICA GEL.

By D. G. R. BONNELL.

Received 7th September, 1931.

Holmes, Kaufmann and Nicholas¹ found that the syneresis of silicic acid gels varied with the hydrogen ion concentration. They showed that the amount of liquid exuded by a gel was increased by the presence of excess of mineral acids while, on the other hand, excess of organic acids retarded the rate of syneresis. The most extreme cases of syneresis were observed with moderately basic gels, with which, in some instances, the quantity of syneretic liquid amounted to 90 per cent. of the original volume of the gel.

Kuhn² observed (a) that weakly basic gels possess a very short setting time and exude liquid very rapidly; (b) that neutral gels set slowly and show weak syneresis; and (c) that with acidic gels the setting time decreased and the syneresis increased as the acidity increased.

Mukoyama,³ during an investigation of the syneresis of viscose gels, found that increasing the alkali content decreased the syneresis.

Ferguson and Appleby⁴ concluded from their results that the setting time of silica gels increased with increasing acidity. Furthermore, the initial velocity of syneresis was greatest with alkaline gels, but at the final equilibrium—which in these cases was attained relatively rapidly—the volume of liquid exuded was less than with acidic gels.

The following is an account of a systematic study of this subject as applied to silicic acid gels.

Experimental.

In the investigation of the effect of hydrogen ion concentration on syneresis, care must be exercised that the silica concentration is constant throughout the series of gels compared. That this is essential is seen from the results discussed in Part I. of this investigation, which show that variations in silica concentration of the gel cause variations in the progress of syneresis. For this purpose, the following procedure was adopted:—

A standard sol, of the highest p_H value to be investigated, was made from known volumes of acid and sodium silicate solutions. A series of sols, differing in hydrogen ion concentration, but of constant silica content, could be prepared by gradually increasing the acid content of the standard sol. This was done by varying the concentration of the acid employed. The p_H of the resulting sols was determined by means of the B.D.H. universal indicator, which allows an accuracy of 0.5 unit of p_H .

The method employed for the determination of the syneresis is fully described in the previous communication on the subject. The temperature was kept constant at 20° C., while the gels were prepared from sodium silicate and hydrochloric, acetic, and sulphuric acids of the same purity as in Part I.

¹ *J. Am. Chem. Soc.*, 41, 1329, 1919.

² *Koll. Z.*, 46, 306, 1928.

³ *Ibid.*, 42, 79, 1927.

⁴ Rept. of the Building Res. Board, p. 56, 1928; *Trans. Faraday Soc.*, 26, 642, 1930.

The experimental results are given in Table I.

TABLE I.

P_H	Induction Period (secs.).	Setting Time (secs.).	Time in Hours after Setting.	Wt. of Liquid in grms. Synerised per 100 grms. gel.
<i>Gels prepared with hydrochloric acid. Silica concentration 6.5 per cent.</i>	4.5	180	1.75	5.537
			2.75	7.023
			6.25	8.655
			18.25	13.228
			26.25	13.489
			67.75	14.750
			71.75	15.012
			95.75	15.614
			162.75	16.238
	10.0	30	1.0	6.325
			5.0	8.955
			46.0	12.735
			70.0	13.225
	7.7.5	5	3.0	9.975
			7.0	11.325
			23.0	12.975
			72.0	13.905
			121.0	14.000
	8.0	5	1.0	5.000
			3.0	9.880
			23.0	12.330
			47.0	12.555
			95.0	12.965
	10.5-11.0	60	1.0	7.550
			2.0	10.405
			6.0	15.510
			23.0	24.135
			48.0	30.445
			96.0	37.235
<i>Gels prepared with hydrochloric acid. Silica concentration 7.5 per cent.</i>	10.0	10	1.0	3.980
			2.5	5.210
			4.0	5.920
			23.0	10.745
			47.5	11.805
			71.0	12.050
	10.5	40	1.0	18.340
			3.0	46.655
			15.0	67.987
			26.0	72.850
			50.5	80.050
			72.0	82.255
	6.5-7.0	10	1.0	5.050
			2.0	6.610
			5.0	7.540
			23.0	8.865
			55.0	9.020
			79.5	9.150
			103.25	9.190
			176.0	9.545

TABLE I. (Cont.).

p_H	Induction Period (secs.).	Setting Time (secs.).	Time in Hours after Setting.	Wt. of Liquid in grms. Synerised per 100 grms. gel.
<i>Gels prepared with hydrochloric acid. Silica concentration 7.5 per cent.</i>	5.0	960	2.5	2.674
			19.0	11.360
			43.5	14.095
			47.0	14.955
			72.0	15.720
			119.75	16.560
			143.75	16.760
	11.0	390	1.25	26.650
			3.0	46.805
			19.0	83.910
			67.0	88.335
			143.0	89.750
<i>Gels prepared with hydrochloric acid. Silica concentration 9.0 per cent.</i>	10.0	5	1.0	8.870
			2.0	14.035
			4.25	16.110
			6.0	18.140
			11.0	21.530
			23.5	28.055
			47.75	34.335
			54.25	35.700
			74.0	38.405
	10.5	60	121.0	42.70.1
			1.0	18.935
			3.0	39.955
			4.75	52.755
			7.0	60.380
			23.0	78.720
			29.75	80.545
			49.30	82.890
			56.25	83.485
			96.3	84.450
<i>Gels prepared with acetic acid. Silica concentration 8.8 per cent.</i>	8.0	5	1.75	9.234
			19.5	11.915
			43.5	12.440
			74.0	12.688
			143.5	12.688
	10.0	10	1.5	9.279
			3.0	10.405
			22.0	12.622
			50.0	13.486
			94.0	14.125
			142.0	14.538
	10.5	20	2.75	10.861
			5.75	14.940
			22.5	23.096
			49.0	29.422
			94.5	36.039
			119.25	38.494
			215.5	45.776
			268.5	48.565

TABLE I. (Cont.).

pH	Induction Period (secs.).	Setting Time (secs.).	Time in Hours after Setting.	Wt. of Liquid in grms. Synerised per 100 grms. gel.
<i>Gels prepared with acetic acid. Silica concentration 8.8 per cent.</i>	5.0	30	3.0	12.071
			5.0	13.768
			23.25	17.542
			46.5	18.709
			76.5	19.176
			218.5	20.132
			383.0	20.537
	3.0	120	3.25	10.687
			5.5	13.067
			23.0	18.448
			48.0	20.944
			72.0	22.030
			126.0	22.897
			195.0	23.874
			294.0	24.780
			359.0	25.651
<i>Gels prepared with sulphuric acid. Silica concentration 8.8 per cent.</i>	8.0	3	1.0	13.174
			5.25	16.932
			29.0	18.410
			47.0	18.579
			70.0	18.748
	10.0	9	1.5	9.813
			3.0	11.070
			20.0	13.961
			47.0	15.247
			116.5	16.266
	10.5	15	160.5	16.842
			5.0	7.245
			22.25	15.353
			70.5	22.558
			95.0	25.235
	11.0	120	143.0	28.562
			1.0	2.776
			2.25	4.654
			20.5	20.069
			46.0	29.634
			74.0	36.123
			118.0	42.066
	4.5	35	168.0	46.286
			247.0	51.155
			3.0	10.866
			5.0	12.901
			22.5	17.380
			46.25	18.829
			100.75	19.911
			169.5	20.396
			266.0	20.731
			334.0	20.790

Analyses of the syneretic liquids in the above experiments showed that in the case of acidic gels, the silica concentration never amounted to more than traces. This was not the case with the alkaline gels. With

those of a weakly basic character the silica content of the synereticum was still negligible, but increased as the alkalinity increased. A further factor influencing the silica content of the syneretic liquid is the silica concentration of the initial gel. With basic gels of *e.g.*, p_H 10.5, the silica content of the exuded liquid varied from 3.0 per cent. for gels of initial silica concentration 9.0 per cent., to 1.5 per cent. for initial concentration 6.5 per cent. Gels could be prepared whose syneretic liquid contained sufficient silica to set into a gel when a little barium chloride solution was added.

As far as could be ascertained, no variation occurred in the silica content of the exuded liquid of any one gel during the time of syneresis.

The silica thus present is, probably, mostly in the form of soluble silicate, and does not seem sufficient to explain the large increase in the volume of liquid syneresised at high p_H values.

A typical example of the curves obtained from the above results is given in Fig. 1.

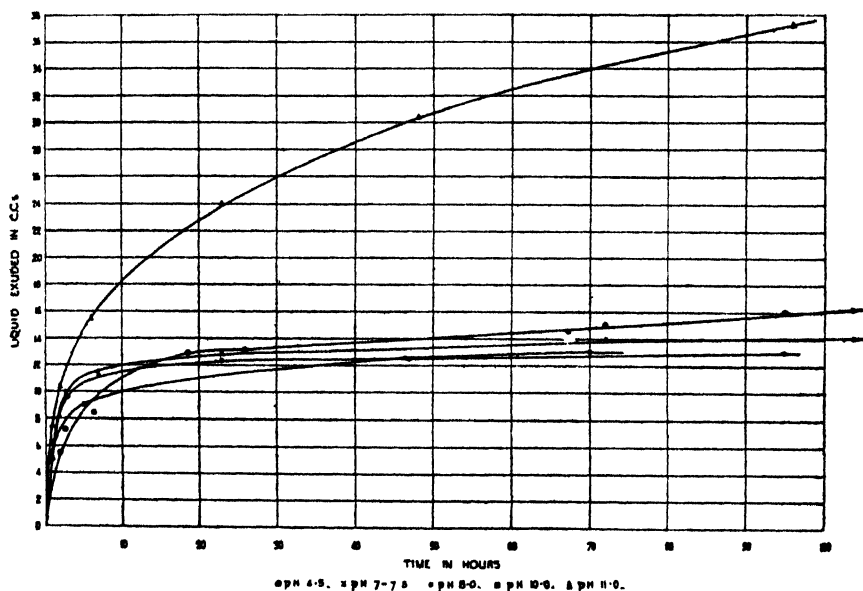


FIG. 1.

Discussion of Results.

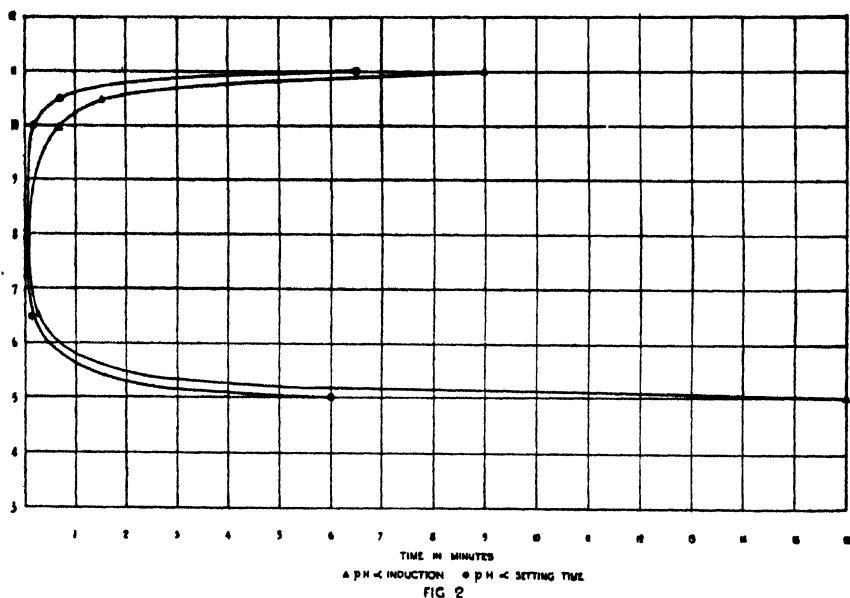
The above results show quite clearly that the hydrogen ion concentration exercises a strong influence on the progress of syneresis of silica gels, both the velocity of exudation and the final equilibrium being affected. The total volume of liquid exuded by syneresis is least with those gels whose p_H lies in the neighbourhood of 8.0. As the p_H of the gel moves in either direction, away from this value, the total volume of the synereticum increases, the increase being greater on the alkaline than on the acidic side. On the other hand, for gels of lower p_H than 11.0, the initial velocity of syneresis increases with increasing p_H up to the value 8.0 and then decreases as the p_H further increases. This does

not seem to hold for gels of p_H 11.0 and higher, as in these cases the initial velocity may be as great as with gels of p_H 8.0.

The general results, therefore, indicate the presence of a definite critical point at a p_H 8.0. While on the one side of this point the variation of the hydrogen ion concentration exercises a certain effect, on the other side the effect is in the reverse direction, *e.g.* below p_H 8.0, the initial velocity increases and the total volume of liquid decreases with increasing p_H , while above this point the velocity decreases and the final volume of liquid increases in the same direction.

The results obtained for p_H values around this critical point show that, in this region, the gel is not very sensitive—as measured by syneresis—to small variations of p_H .

The above conclusions are corroborated by the following information on the influence of the hydrogen ion concentration on the setting time



of the gel and on the period of induction which elapses before syneresis commences. The data are collected in Table II, and a typical example of the curves obtained is shown in Fig. 2.

An analysis of the table and figure again shows the presence of a critical point in the neighbourhood of p_H 8.0. Although both the setting times and the periods of induction increase as the p_H of the gel recedes in either direction from 8.0, nevertheless the change does not take place suddenly, but, gradually over the small range of 7.0 to 9.0. The variation over this range is so small as to make the setting time and the induction period practically independent of the hydrogen ion concentration. Interpolation on the curves show the points of minimum setting time and period of induction, for the investigated silica concentrations, to be between 7.5 and 8.0 p_H . This point seems to be independent of the coagulant used.

Prasad and Hattiangadi⁵ during their investigations of the setting of silica gels, observed a similar behaviour. They obtained minimum setting times at p_H values, varying between 7.2 and 7.8, depending on the silica concentration of the gel.

From theoretical considerations the minimum setting time should occur at the isoelectric point. This would imply that the isoelectric point in the gels investigated does not occur at the neutrality value of p_H 7.0, but at a value slightly on the alkaline side. This agrees also with the conclusions arrived at by Fleming.⁶

TABLE II.

Coagulant.	Per Cent. Silica Concentration.	p_H .	Setting Time in Secs.	Induction Period in Secs.
HCl	6.5	4.5	180	—
		10.0	30	—
		7.0—7.5	5	—
		8.0	5	—
		10.5	60	—
HCl	7.5	11.0	390	540
		10.5	40	90
		10.0	10	39
		6.5—7.0	10	15
		5.0	360	960
CH ₃ COOH	8.6	10.5	20	60
		10.0	10	15
		8.0	3	5
		5.0	30	60
		3.0	120	300
H ₂ SO ₄	8.8	11.0	120	600
		10.5	15	120
		10.0	9	20
		8.0	3	5
		4.5	35	90

This effect was not recognised by Ferguson and Appleby, due to the fact that most of the hydrogen ion concentrations investigated lay on one side of the isoelectric point.

Effect of Temperature on Syneresis.

Ferguson and Appleby⁴ found that the syneresis of silica gels increased with increasing temperature. The experiments tabulated in Tables III. and IV. were carried out with gels prepared with hydrochloric and acetic acids for further corroborative evidence on this effect.

It will be seen that the phenomenon is not only accelerated, but also proceeds to a further stage with increasing temperature. This indicates that the higher temperature facilitates the contraction of the gel, possibly through the decrease in the viscosity of the dispersion medium. These results agree entirely with those found by Ferguson and Appleby.⁴

⁵ *J. Indian Chem. Soc.*, VI, 893, 1929. ⁶ *Z. physik. Chem.*, 41, 427, 1902.

TABLE III.

Hydrochloric acid gels. Silica concentration, 6.5 per cent.

Temperature 20° C.		Temperature 30° C.	
Time in hrs. after Setting.	Liquid Synerised in grms./100 grms. gel.	Time in hrs. after Setting.	Liquid Synerised in grms./100 grms. gel.
1'75	5'537	1'0	7'151
2'75	7'023	3'0	10'940
6'25	8'655	19'5	16'008
18'25	13'228	43'5	16'548
26'25	13'489	91'5	17'442
67'75	14'750	139'0	17'838
71'75	15'012		
95'75	15'614		
162'75	16'238		

TABLE IV.

Acetic acid gels. Silica concentration, 8.8 per cent.

The time is expressed in hours after setting, and the liquid exuded in grams per 100 grams of gel.

Temperature 20° C.		Temperature 30° C.		Temperature 40° C.	
Time.	Liquid.	Time.	Liquid.	Time.	Liquid.
1'75	9'234	1'66	11'318	1'0	11'50
19'5	11'915	3'0	12'638	3'5	14'825
43'5	12'440	5'0	13'213	5'7	15'240
74'0	12'688	22'5	14'450	23'5	16'349
143'5	12'688	52'0	14'600	47'25	16'695
				147'25	17'003
				216'25	17'215

Summary.

The effect of the hydrogen ion concentration of the gel on the phenomenon of syneresis of silica gels of various concentrations over a wide range of p_H values has been investigated.

The data obtained for the setting time and periods of induction indicate that the iso-electric point, for silica gels of the concentrations studied, lies between p_H 7.5 and 8.0.

The effect of temperature on syneresis has also been investigated.

The author wishes to express his thanks to the Director of Building Research for kind permission to publish these results, and to Mr. B. H. Wilsdon for many helpful suggestions.

*Building Research Station,
Bucknall's Lane,
Garston, Herts.*

AN IMPROVED SEDIMENTATION METHOD FOR THE DETERMINATION OF PARTICLE SIZES, USING AN AUTOMATIC RECORDER.

By C. G. SUMNER.

Received 6th October, 1931.

The "sedimentation tube" method of determining the size distribution of particles in suspension consists in allowing the particles to sediment in a vertical tube which is provided with an open capillary side tube containing a suitable index liquid. The passage of particles past the orifice of the side tube (upwards or downwards as the case may be) produces, in the liquid contained in the main tube above this junction, a decrease in density proportional to the mass of particles sedimented. This change is recorded by a downward movement of the index liquid, and by determining the latter movement as a function of time, an accumulation curve may be plotted, whence the size distribution of the particles is calculable by use of Stokes' law.

Such a sedimentation tube was first used by Wiegner,¹ and modified by Ostwald and Hahn.² It was considerably improved by Kelley,³ who bent the side tube, at a point nearly level with the surface of the suspension, into a nearly horizontal position. In this way, the movement of the meniscus is considerably magnified. A similar tube, adapted for systems in which the disperse phase is lighter than the medium, was used by Kraemer and Stamm.⁴ Lambert and Wightman⁵ described a means of recording the movement of the index photographically, and the present paper relates to improvements in the technique and theory of this method. All these experiments refer to suspensions in aqueous media.

The Sedimentation Tube.

The principal difficulty attending the use of a tube of this type is in obtaining free movement of the index. Previous workers have used water, or an aqueous solution of low surface tension, as the index liquid, but the difficulty of eliminating sticking with a water meniscus is well known, and considerable improvement has been effected by the writer by employing benzene. For this purpose a side tube is used, having the form shown in Fig. 1. The tube is in two sections, the joint being sealed by a short piece of rubber pressure tubing. The capillary attached to the vertical tube A is filled with dispersion medium (water or solution), while the index tube proper (B) contains benzene. The boundary between the liquids is in a wide cylindrical bulb C such that, for a movement of the index meniscus over its whole range, the movement of the boundary is accommodated within the cylindrical portion of the bulb. Since only *changes* in hydrostatic pressure are involved, the exact position of the boundary, when the tube is set up, is immaterial.

¹ Wiegner, *Landw. Versuchsstat.*, **91**, 41, 1919.

² Ostwald and Hahn, *Kolloid-Z.*, **30**, 62, 1922.

³ Kelley, *Ind. Eng. Chem.*, **16**, 928, 1924.

⁴ Kraemer and Stamm, *J. Amer. Chem. Soc.*, **46**, 2709, 1924.

⁵ Lambert and Wightman, *J. Opt. Soc. Amer.*, **11**, 393, 1925.

The side tube is provided with a bulb D containing benzene, in order to minimise evaporation from the index meniscus. For a similar purpose the vertical tube A is provided with a special cap F, as described by Kelley. This has a small vent and incorporates a reservoir for the appropriate liquid. The tube illustrated is adapted for a rising disperse phase (after Kraemer and Stamm), and principal dimensions of the writer's example are given in the diagram. The capillary tube has a bore 2 mm. in diameter.

The components of the apparatus are cleansed separately in chromic acid mixture and washed with distilled water before use. The detachable side tube is then washed with alcohol or acetone and dried by drawing air through it. By careful suction and manipulation of the tap E, the tube B and upper portion of the bulb C are filled with benzene, the lower portion of C with solution; during this operation benzene is drawn over into the bulb D. With the tap closed, the side arm is attached to the main tube as shown; by manipulation of E the liquid is allowed to run back until it reaches the vertical tube. In order to avoid air bubbles, the bore at the lower end of the detachable side tube is bell-mouthed. The benzene level is maintained near the top by allowing sufficient liquid to run back from the reservoir C.

The apparatus is then fixed in position in the thermostat, and allowed to reach temperature equilibrium. The suspension, previously brought to the correct temperature, is run into the vertical tube to a suitable height, E is opened, and recording is begun.

With an aqueous liquid as the index, trouble due to sticking was experienced, and the movement exhibited considerable lag, but with benzene sticking is eliminated, and the index is much more mobile (see later).

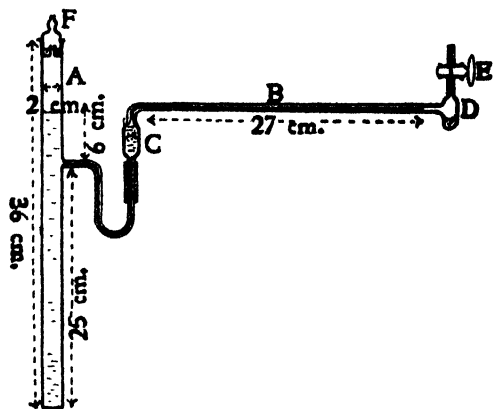


FIG. 1.—Sedimentation tube.

The Recorder.

The recording camera is essentially similar to that described by Lambert and Wightman.⁵ It comprises a box containing three rollers, whose axes are parallel to the side tube, arranged approximately in a vertical plane (see Fig. 2). Bromide paper from the bottom roller R_1 passes over the top roller R_2 , which is an idler, and is wound on to the middle roller R_3 . A light source placed vertically above the tube is illuminated periodically for a suitable fraction of time, and the optical action of the tube is such that an image of the liquid column is projected on to the sensitive paper through a slit on the top of the box. The record thus obtained gives the position of the index as a function of time. Measurements on the record are based on a reference line obtained by fixing a piece of fine wire across the slit at the lower end. The action of the camera is automatic.

An improved method of operating the camera has been described by the writer in a separate paper.⁶ The motor for winding the exposed paper comes into operation only after an exposure has been made, for sufficient time to bring a new portion of paper into the field. In consequence a wide range of exposure frequencies may be provided, the apparatus described allowing of intervals of 1, 10, 20, 30, or 60 minutes between exposures. The frequency of exposures is varied according to the rapidity of sedimentation, and even during a single "run" may be decreased as the movement slows down.

The apparatus is set up in a light-tight air thermostat regulated to within 0.1° C. of the desired temperature (25° C. in this case), and the arrangement adopted by the writer is shown in Fig. 2. The baseboard A carries a vertical pillar B, to which the sedimentation tube is attached,

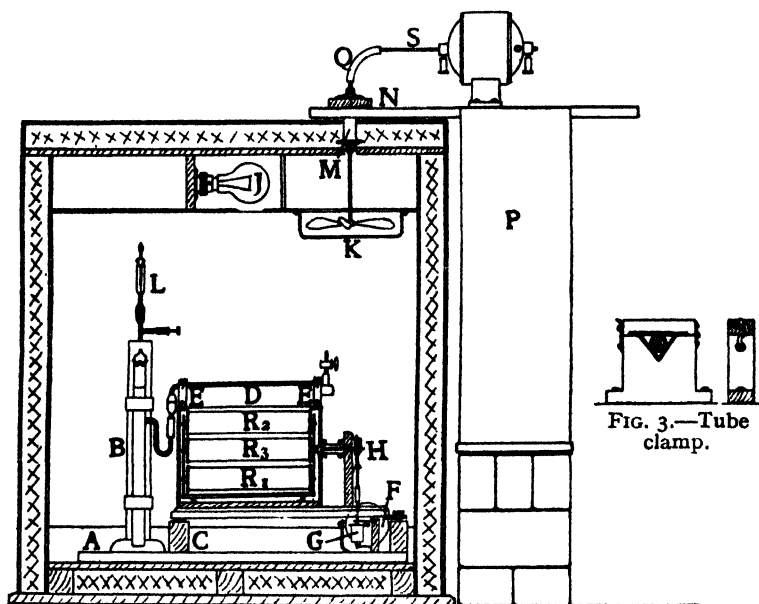


FIG. 2.—Arrangement of sedimentation apparatus.

and transverse blocks C on which rest (in slight depressions) the levelling screws of the camera D. The side arm of the sedimentation tube is supported in two wooden V-blocks E, which are fastened to the camera box. These blocks are lined with felt and have a hinged clamping member secured by a hook, the whole being made to fit the tube, without shake but without strain. (See Fig. 3.) Similar blocks are used to hold the vertical tube to the pillar. By this means the tube may be placed in position quickly and reproducibly. The rubber joint in the side arm enables the latter to be set at any convenient angle by adjustment of the camera alone, since the tube is attached to the camera and is always parallel to it. This direct attachment is made practicable by the discontinuous action of the camera, for since the winding motor is in operation for only a few seconds after each exposure, the vibration is negligible.

⁶ Sumner, *J. Scientific Instruments*, 8, 104, 1931.

The front of the camera is detachable, and the rollers are mounted in a frame which slides into the box between guides. Attachment of the middle roller to the winding shaft is by means of a dog clutch. The driving motor F is fastened to the floor of the thermostat, and drives the roller through two consecutive worm gears. The first gear G is mounted below the camera stand, similarly to the motor (the baseboard A being cut to accommodate it), and the second gear H is arranged on the stand itself. Details of the arrangement are given in the previous paper.

The illuminant is a 60-watt gas-filled lamp J, enclosed in a box which has a slit about 2 mm. wide, parallel to the side tube. The filament of the lamp is transverse to the slit, so that an approximation to a point source is obtained; this gives a sharp image. The slit is long enough for the whole length of the tube to be illuminated. The side tube is so disposed in relation to the paper and illuminant as to give the best image, this position being found by experiment. The duration of each exposure is $1\frac{1}{2}$ seconds. With benzene the image is less intense than with water, but there is sufficient contrast for measurement. The paper used is Wellington Platino-Matt, single weight, 10 inches wide.

The thermostat comprises a lagged, double-walled box fitted with partitions so as to form a flue at the back, communicating with a warm air chamber at the top. Air is drawn into the flue at the bottom, which is open to the main enclosure, and passes across the heater, which consists of a grid of nichrome wire arranged in the flue. The warm air rises into the top compartment, whence it is driven downwards into the experimental enclosure by a fan K working just below an opening in the partition. A positive air circulation is thus maintained. The thermo-regulator L is supported at the rear of the pillar B; for temperature control an improved circuit, described elsewhere by the writer,⁷ is used. The fan bearing is a cycle hub M attached to a board N, which is arranged just clear of the top of the thermostat. N in turn is carried from a resilient structure P built alongside the thermostat. The flexible drive Q from the extended motor shaft S consists of rubber pressure tubing. In this arrangement no part of the fan system is directly attached to the thermostat, and vibration is minimised.

Calibration.

The relation between the position of the index meniscus and the mass of particles sedimented is obtained by calibration, following the method of Lambert and Wightman. The vertical tube is filled with pure dispersion medium (water or solution), until the index stands near the upper limit of the range, and the recorder is started, exposures being made once per minute. Successive portions of liquid are then withdrawn in a weighed pipette of suitable form, and determined by weighing, until the index reaches the lower limit of the range. Time is given after each withdrawal for equilibrium to be regained.

The record so obtained shows the relation between displacements of the index, *on the paper*, and changes in hydrostatic pressure; also the speed with which equilibrium is regained. The desired relation with the mass of particles sedimented, which is derived at length by Lambert and Wightman, may be obtained very simply as follows.

⁷ Sumner, *ibid.*, 7, 398, 1930.

24 METHOD FOR DETERMINATION OF PARTICLE SIZES

The movement due to a given decrease in hydrostatic pressure is entirely independent of how the change is produced. If, therefore, a displacement between two given points is produced (a) by withdrawal of δW gms. of water, (b) by sedimentation of δP gms. of particles, these two changes are equivalent. Let ρ_p, ρ_w be the densities of particles and medium respectively, A the cross-section of the main tube. In sedimentation, $\delta P/\rho_p$ c.c. of particles are replaced by the same volume of medium; the corresponding change in pressure is therefore $\delta P/A\rho_p(\rho_p - \rho_w)$ gms. per sq. cm. Hence we have

$$\frac{\delta P}{A\rho_p}(\rho_p - \rho_w) = \frac{\delta W}{A}$$

$$\text{or} \quad \delta P = \delta W \left(\frac{\rho_p}{\rho_p - \rho_w} \right) \quad . \quad . \quad . \quad (1)$$

From the record and weighings a calibration curve may be plotted by means of this relation, giving δP as a function of the recorded length. With a uniform straight tube, if there were no parallax error this relation would be linear. In view of the error a slight curvature is to be expected, but with the particular tube described, it is found that no appreciable deviation from a straight line occurs.

In the experiments described by Lambert and Wightman, each sedimentation experiment is accompanied by a calibration. In a series of consecutive experiments, this is unnecessarily tedious, as it is found that the position of the apparatus is reproducible within the accuracy of experiment. It is therefore sufficient to use the same curve for a number of experiments, although it is advisable to check the calibration from time to time. A composite curve may be derived from a number of independent calibrations, which are arranged to overlap so as to obtain values at more points in the range of movement than is possible in a single experiment. The separate curves are compared by measuring values against l on a common graph, a "best curve" may be drawn, the value of dP/dl at various values of l . By plotting these dP/dl δP over any range being obtained by integration of the area under the curve.

Correction Due to Viscosity.

As has been pointed out by Lambert and Wightman, there is a lag in the movement of the index, due to its viscosity. The method of correction described, however, is not strictly accurate, and a simpler method is due to the writer.

Considering the calibration curve, let $\dots l_0, l_0, l_1, l_2 \dots l_n \dots l, l, \dots$ be the lengths of column at successive minutes, l_0 and l being the equilibrium values before and after the withdrawal of δW gms. of solution. In the interval l_n to l_{n+1} , the mean effective pressure P will be proportional to $\frac{1}{2}(l_n + l_{n+1}) - l$, and the velocity will be $(l_n - l_{n+1})$ per minute. We have then

$$(l_n - l_{n+1}) \propto P/X,$$

where P/X is the effective pressure gradient. X will vary with the position of the index meniscus; for a small movement it will be sensibly constant, and

$$(l_n - l_{n+1}) = \frac{1}{k} \left[\frac{1}{2}(l_n + l_{n+1}) - l \right] \quad . \quad . \quad . \quad (2)$$

where k is constant. k may be evaluated by plotting $(l_n - l_{n+1})$ against $\left(\frac{l_n + l_{n+1}}{2} - l\right)$ for successive points. Since it involves X , some variation over the range of the index tube is to be expected.

Multiplying across by k and adding $\frac{1}{2}(l_n - l_{n+1})$ to both sides, we get

$$(k + \frac{1}{2})(l_n - l_{n+1}) = l_n - l \quad (3)$$

This is equivalent to the relation used by Lambert and Wightman. It is not permissible, however, to assume that it holds also for the sedimentation values, as is done by these authors. During sedimentation, the point of equilibrium for the index is moving continuously, and at any instant the lag of the meniscus behind its true position will be such that the pressure difference, due to the lag, suffices to impart to the liquid its observed velocity. Let l_n, l_{n+1} be the observed lengths of column at successive minutes, and l'_n, l'_{n+1} the corresponding true values. The mean lag of the meniscus in the interval will be $\frac{1}{2}(l_n + l_{n+1}) - \frac{1}{2}(l'_n + l'_{n+1})$, the observed velocity $(l_n - l_{n+1})$ per minute. Then we have

$$k(l_n - l_{n+1}) = \frac{1}{2}(l_n + l_{n+1}) - \frac{1}{2}(l'_n + l'_{n+1}) \quad (4)$$

That is, the mean lag is equal to k times the distance moved in the minute, *i.e.*, to the distance moved in k minutes if the speed is uniform over this range of time. This will be true at the beginning of the experiment, where also the error is most significant, since the movement is most rapid, and if k is small, it will hold closely for other points also. In other words, the meniscus should have reached its observed position k minutes before it actually does so. Applying this principle to the whole curve, it is evident that the corrected curve may be obtained from the observed curve by keeping the lengths unaltered and decreasing the time values by k minutes.

The significance of this correction depends on the rate of sedimentation; in all cases, however, it is offset by the fact that zero time on the record does not, in general, correspond with the actual beginning of sedimentation, but with some later time, depending on the time of pouring the suspension into the main tube. It may be assumed that the process of sedimentation starts when agitation of the suspension ceases. If, therefore, conditions are arranged so that pouring of the suspension into the tube is completed approximately k minutes before the first exposure occurs, the record itself will have a lag practically equal to that of the meniscus. The error in taking the record without correction then becomes negligible. With the writer's apparatus, it is found that k is of the same order over the whole range of the index tube, so that this is valid for the complete record. The first reading on the record may be unreliable, but the correct value is readily obtained by extrapolation.

In the apparatus described, using benzene as the index liquid, a new equilibrium in a calibration is nearly reached within one minute of withdrawing a quantity of solution, so that from (3), k is of the order $\frac{1}{2}$. With water, a new equilibrium had not been reached in five minutes after withdrawal. This difference is greater than can be attributed to the higher viscous resistance with water, and was probably due to surface tension effects, since sticking trouble was experienced also. Owing to the low surface tension of benzene, and the solvent action of the liquid on grease, trouble of this kind is not encountered in the

26 METHOD FOR DETERMINATION OF PARTICLE SIZES

improved apparatus. A record of the meniscus in a steady state shows quite slight random variations about a mean position.

If to both sides of (4) we add $\frac{1}{2}(l_n - l_{n+1}) + \frac{1}{2}(l'_n - l'_{n+1})$, which is equal to $(l_n - l_{n+1})$ if the speed is uniform, we obtain

$$(k+1)(l_n - l_{n+1}) = l_n - l'_{n+1} \quad (5)$$

which differs from the expression

$$(k + \frac{1}{2})(l_n - l_{n+1}) = l_n - l'_{n+1} \quad (6)$$

used when applying (3) to the sedimentation values, as suggested by Lambert and Wightman. The latter correction is too small by

$$\frac{1}{2}(l_n - l_{n+1}).$$

Derivation of Distribution Curve.

A curve showing the mass distribution of the particles over the range of sizes may be derived as follows. Let P be the total mass of particles which have passed the orifice in time t from the beginning of sedimentation. If h is the maximum distance to be traversed by the particles (*i.e.*, the distance of the orifice from the upper or lower surface of the liquid, according as $(\rho_p - \rho_w)$ is positive or negative), then after time t all particles having velocities greater than h/t will have settled out completely; let the total mass of such particles be S . Then it may be shown readily that

$$S = P - t \frac{dP}{dt} \quad (7)$$

The sedimentation record (in conjunction with the calibration curve) gives the (P, t) curve, and from this the values of S at various t values may be obtained by drawing tangents to the curve at the appropriate points. The intercept cut off the P axis by a tangent is evidently $(P - t \frac{dP}{dt})$, which is equal to S by equation (7). This method is described by Svedberg.⁸

If r is the radius of particles having the velocity h/t , we have by Stokes' law

$$h/t = \frac{2}{9}g \left(\frac{\rho_p - \rho_w}{\eta} \right) r^2 \quad (8)$$

$$\text{or} \quad r^2 = \frac{9}{2} \cdot \frac{h\eta}{g(\rho_p - \rho_w)} \cdot \frac{1}{t} = \frac{c}{t} \quad (9)$$

where η is the viscosity of the medium and g the gravity constant.

A curve may be plotted, having either S or dS/dr as ordinate and r as abscissa, by deriving S or δS from the (P, t) curve as described, and the corresponding r and δr values by use of equation (8). dS/dr is taken as the value of $\delta S/\delta r$ at the middle of the interval. Previous workers have used the values corresponding to equal intervals of *time*, but a considerable saving in calculation, in the case of the differential curve, is achieved by working in terms of equal intervals of *radius*. The times corresponding to $\delta r, 2\delta r, \dots, n\delta r, \dots$ are calculated from equation (8), and tangents to the (P, t) curve are drawn at the calculated points. The $\delta S/\delta r$ values may be plotted against r as before, or the δS values read off may be

⁸ Svedberg, *Colloid Chemistry*, 1928, p. 176 *et seq.*

plotted against $n(=r/\delta r)$. In either case integration of the area under the curve gives S over the range in question; the latter method is, however, less laborious.

It is convenient in many cases to use the fraction S/S_∞ , where S_∞ is the quantity corresponding with complete sedimentation. If the calibration curve of the apparatus is linear to within a sufficient degree of accuracy, S/S_∞ is equal to the ratio of the corresponding lengths of column. In such a case, it is unnecessary to use the calibration at all; the curve is plotted in terms of length instead of mass. Where this does not hold, or where the mass of particles is wanted, the calibration must be used.

It is to be noticed that no correction is necessary for a *uniform* downward drift of the index, due to evaporation. The effect of this is to increase the apparent values of P and $t \frac{dP}{dt}$ by equal amounts, so that the derived S values are independent of the error. Such a slight drift is actually observed.

This method was developed in the "Thomas Graham" Colloid Research Laboratory in the Victoria University of Manchester. Thanks are due to Mr. D. C. Henry, director of this laboratory, for facilities afforded, and also to the Department of Scientific and Industrial Research for a Senior Research Award.

Summary.

An improved technique, developed from the method of Lambert and Wightman, is described, for applying an automatic recording camera to the determination of particle sizes by a sedimentation tube method. Special features include a tube arranged for the use of benzene as the index liquid, a new design of discontinuous recording camera, and a simple method of correcting for the effect of viscosity in the index tube. Simplified means of deriving the calibration equation and of deducing the size distribution from the experimental record, are also given.

COLLOID CHEMISTRY OF GLIADIN SEPARATION PHENOMENA.

By H. L. BUNGENBERG DE JONG and W. J. KLAAR.*

Received 31st August, 1931.

When preparing flour suspensions in very dilute acid, we observed that, after removing the suspended particles of starch and protein by centrifuging, solutions were obtained which differed from other protein solutions by their cloudiness. It appeared that these turbid solutions could be filtered through ordinary filters without any change in their turbidity. This cloudiness indicated an unusual phenomenon, and, indeed, a microscopical investigation showed that the liquid contained a large number of drops.

* *Laboratory Maatschappij de Korenschoof, Utrecht, Holland.*

These drops did not contain any fat, as was proved by colouring them with various dyes, which would have coloured fat, and it was evident that the drops consisted chiefly of protein. Their liquid nature was further confirmed by filtering through porous crucibles.

We gave the name *separation* to this phenomenon of the formation of a new phase dispersed in the initial phase. Thus, for example, the initial phase may consist of a protein dispersed in water, which may separate to a system of water dispersed in gliadin (the drops) which in turn is dispersed in water.

As the system flour-water-acid was thought to be too complicated, and because one or two of the proteins of the gluten appeared to be the cause of the effect of *separation*, we continued the investigation of this phenomenon with solutions of acid and purified gluten which had been dried *in vacuo*.

We embodied the results in a preliminary communication,¹ and pointed out the connection between this phenomenon of separation and the hydration of the colloidal protein. At the same time a certain analogy between the systems phenol-water and colloidal protein-water was shown in the appearance of a super critical mixing temperature.

These separated solutions appeared to become water-clear above certain temperatures, whereas on cooling down the liquid separated once more. The cloudy separated solutions could be completely cleared up in alcohol of approximately 50 per cent. by weight, while in higher alcohol concentrations the solutions became for a second time cloudy. As the solubility in alcohol of 50 per cent. by weight is a characteristic of gliadin (one of the proteins of the gluten), it was suspected that this protein was responsible for the phenomenon of separation. Therefore we have continued our investigations by studying the properties of gliadin.^{2,3}

Following the directions of other investigators (Osborne, Blish and Sandstedt, Sharp and Gortner),⁴ we have made various preparations of gliadin, which has been purified with the utmost care. It was evident that our supposition was true, and that the protein or proteins called gliadin showed the phenomenon of separation (Fig. 1). Purification by different methods did not have any influence on this phenomenon. Just as with solutions obtained from gluten, so, in this case, the separation was caused by change of charge and of hydration of the protein. This can be brought about not only by the addition of electrolytes and (with acid solutions) of alkali—both of which influence charge as well as hydration—but also by substances that only influence the hydration, e.g., alcohol, acetone or resorcinol.

On closer investigation of the literature it appeared that Osborne, the investigator of the proteins of wheat, also speaks in his book, "The Proteins of the Wheat Kernel," about cloudy solutions of gliadin.

In 1929 Berliner and Koopman⁵ found microscopically protein drops in acid flour suspensions. However, neither of these investigators went any further into the matter.

By the addition of alcohol to a cloudy aqueous gliadin sol, a perfectly water-clear solution was obtained at an alcohol concentration of

¹ *Cereal Chem.*, 6, (5), 373, 1929.

² *Ibid.*, 7, (3), 222, 1930.

³ *Ibid.*, (6), 587, 1930.

⁴ M. J. Blish and R. M. Sandstedt, *Cereal Chem.*, 3, 144, 1926; T. B. Osborne, "The Proteins of the Wheat Kernel," 1907; F. Sharp and R. A. Gortner, *J. physical Chem.*, 27, 481, 1923.

⁵ E. Berliner and J. Koopmann, *Z. ges. Mühlenwesen*, 6, 57, 1929.

48 per cent. \pm by weight. By further increasing the alcohol concentration the cloudiness reappears. The same phenomena could be observed with acetone.

To investigate these phenomena quantitatively we decided to use the viscosimetric method. For this purpose two different kinds of sols were made, firstly, clear colloidal solutions, obtained by addition of a quantity of acid sufficient for complete peptization, and, secondly, sols which were all microscopically separated to a more or less extent. These separated sols were made by adding too small a quantity of acid for complete peptization.

Before discussing shortly the results of the viscosimeter measurements, it is desirable to point out that in colloidal problems the change of hydration of the particles is one of the most important factors. The relative viscosities of these sols were therefore calculated by dividing the viscosities of the alcoholic protein sols (η_{s+A}) by those of the corresponding alcohol-water mixtures (η_A). The value thus obtained ($\frac{\eta_{s+A}}{\eta_A}$) the relative viscosity indicates the change in the value $1 + 5/2\phi$ in the Einstein formula, *i.e.*, the change in the total volume of the particles, including their solvation layers.

From our viscosity determinations, it was evident that by increasing the alcohol concentration in the sol, the relative viscosity of the sol increases, at first, until a maximum is reached in alcohol of about 48 per cent. by weight. By increasing the alcohol concentration beyond this maximum, a sharp decrease in the relative viscosity of the sol occurs. Thus, for instance, in alcohol 80 per cent. by weight a relative viscosity of the sol was reached far beneath the initial value of the aqueous sol. The same effect could be observed with gliadin in acetone-water mixtures. In this case the maximum was found at an acetone concentration of 44 per cent. \pm by volume. The maximal value in the relative viscosity for acetone-water gliadin sols was larger than that for alcoholic gliadin sols, starting from the same aqueous sol.

From the foregoing facts it must follow that, by increasing the alcohol or acetone concentration in a gliadin sol, an increase in the solvation layer ($1 + K\phi$) must take place, until the maximum is reached in the relative viscosity. (We neglect in this reasoning that there can also occur, by changing the composition of the medium from an aqueous to an alcoholic one, a change in the electric term in the formula of von Smoluchowski.)

The increase of the protecting layer by addition of alcohol could be observed microscopically. By starting from a strongly-separated aqueous gliadin sol, the drops could be seen to swell on adding traces of alcohol. By further increasing the alcohol concentration, the outlines of the drops become more and more vague, and finally an optically void liquid was obtained.

Attention must be drawn to the fact that the sols with maximal viscosity, both in alcohol- (or acetone-) water mixtures, show a very high stability. Neither electrolytes nor dehydrating substances, such as resorcinol, have any visible effect on the appearance of the water-clear sol; this may be contrasted with aqueous solutions, where these substances exercise a marked influence on the appearance of the sols. This stability must have its origin in a very special state of the solvation layer, in our opinion this stability must be caused by a layer of alcohol or acetone hydrate molecules.

The decrease in the relative viscosity in higher concentrations of these dispersion media must be caused by a gradual desolvation of the particles, with the result that in practically pure alcohol or acetone the particles must have lost their protecting layer. In these concentrations of alcohol or acetone the sol will be only stable on its charge and is transformed into a suspensoid sol, as indicated by its blue opalescent colour, Tyndall effect, etc.

It appears that the shape of the corresponding viscosity curves with varying alcohol or acetone concentrations are the same for optically clear, as well as for separated sols. However, the percentage rise in viscosity (the difference in relative viscosity between the alcoholic sol at the maximum and the aqueous sol, divided by the relative viscosity of the aqueous sol minus 1, *i.e.*, the percentage increase of the total volume of the particles (ϕ)) is much larger for separated sols.

We next investigated the manner in which this percentage rise changed with the acidity of the initial sol. We found that, starting from a separated sol, by increasing the charge of the particles, this percentage rise decreases until a minimum was reached at an acid concentration in the sol, whereat the aqueous sol has its maximal viscosity. On increasing the acid concentration beyond this point, a slight drop in this value occurs at first. At still higher acid concentrations the percentage rise increases, finally reaching very high values. Here, in an aqueous medium, a second area of separation could be observed, while the alcohol sols were all perfectly clear. As the shape of the curve, showing the percentage increases plotted against the viscosities of aqueous sols at different p_H , is perfectly regular, it follows that separation is a gradual, continuous process in the microscopically visible, as well as in the amicroscopical area. Therefore separation does not occur abruptly at a definite state of charge of the particles.

We will now briefly discuss the separation of gliadin. These phenomena are influenced by the following factors: (a) the charge of the particles, (b) the hydration of the particles, (c) the composition of the dispersion medium, (d) the temperature, (e) the presence of surface active material, (f) lyotropic effect of electrolytes.

The following illustrations will make this clear:—

(1) *Variable charge of the particles in aqueous medium, constant temperature.*—(This effect is coupled with the lyotropic effect (f) in aqueous medium, see page 31).

(i) By a decrease of charge of the particles in a clear gliadin sol, either by a change in p_H of the sol or by addition of electrolytes, the liquid separates into a number of small drops. By further decreasing the charge of the sol an enlargement of these drops will occur.

(ii) So long as the particles are charged, the visible drops do not run together.

(iii) By total discharging (*i.e.*, iso-electrically) the drops stick together and form strings. Conversely, starting from a thread of gliadin in water, the thread is seen to expel from its surface a number of small drops when dilute acid is added. The drops spread into the surrounding liquid, and gradually melt away.

(2) *Variable medium, constant temperature and constant charge on the particles.*

(i) Separated sols gradually become water-clear, when substances are added which increase the solvation of the particles (acetone and different alcohols up to a certain concentration).

(ii) Higher concentrations of these solvents exercise a desolvating influence on the particles and a second separation effect can be observed.

(3) *Variable temperature, constant charge on the particles, aqueous medium.*

(i) Separated sols become water-clear by increase of temperature of the sols.

(ii) Clear sols become turbid on cooling down.

(4) *Variable temperature and charge, aqueous medium.*

The higher the charge of the sol particles, the lower will be the temperature at which visible separation occurs. The curve obtained by plotting these turbidity temperatures against the acid concentration, has the same shape as the viscosity acid concentration curve.

(5) *Variable temperature and medium, constant charge of the sol.*

By increasing the solvation of the particles by change of medium, as indicated by an increase in viscosity of the sol, the temperature at which visible separation occurs will be decreased. Therefore, a sol with maximal viscosity in alcohol-water has a higher turbidity temperature than the same sol with maximal viscosity in acetone-water.

(6) *Variable charge, constant temperature, constant medium (acetone-water).*

By decreasing the charge of clear acetone-water gliadin sol, cooled to low temperatures, a turbidity occurs.

(7) *Surface active substances.*

Clear aqueous gliadin sols can be separated by addition of somewhat high concentrations of resorcinol. In aqueous solutions, containing still higher concentrations of resorcinol, a clearing of the turbid liquid takes place.

Before passing on to the discussion of the effects of separation of colloids in general, there is a matter which deserves attention. On page 28 we compared the separation of colloids with the separation of the system phenol-water. This comparison holds good only superficially, and, strictly speaking, it is not true.

From solubility determinations it was evident that we cannot apply the phase-rule to a separated gliadin system, at least if we consider the gliadin as a one-component system. This fact is in accordance with the effects found by several investigators among others, Ostwald and his collaborators,⁶ who have vainly tried to apply the phase-rule to colloid systems.

By the discharging of colloidal solutions at normal temperature, two extreme possibilities can occur. (1) The remaining hydration of a discharged colloid can be so large that the whole system remains in solution; or (2) the discharged particles are absolutely free from solvate molecules, in which case the system will flocculate into a solid sediment. Between these two extremes a number of intermediate cases can be found. In these cases the sediment will bind in an uncharged condition more or less solvate molecules.

The proteins gelatin and albumin represent the first mentioned case. Both these proteins remain in solution iso-electrically under normal conditions (*i.e.*, normal temperature and in the absence of dehydrating substances).

On the other hand, by the discharging of glutenin and casein, a very fine flocculation can be obtained that microscopically shows a more or less solid nature (Fig. 2).

⁶ Wo. Ostwald und R. Köhler, *Koll. Z.*, **43**, 131, 1927.

In gliadin and in general in the prolamins we have a number of proteins, the properties of which stand between these two extreme cases. Here the semi-liquid nature of the sediment indicates a relatively high degree of hydration of the uncharged particles. This hydration, however, is not sufficient to keep the protein in solution. In our opinion, this degree of solvation determines whether a protein will flocculate, or separate, or remain in solution in uncharged condition, under normal circumstances. If this supposition is right, the possibility must exist of forcing a protein into every possible form of sediment by influencing its solvation. Several phenomena point in that direction. For example, we have succeeded, by the addition of substances which enlarge the solvation of the particles, in *separating* glutenin and casein which normally flocculate. On the other hand, albumin can be caused either to separate or to flocculate through a decrease of hydration. In gliadin we have a protein in which different forms of sediment can easily be realised by change in solvation. These changes can be brought about at normal temperature by different alcohol or acetone concentrations.

For instance, uncharged gliadin, which in aqueous medium forms a semi-solid sediment, gives, on addition of alcohol, sediments of an increasingly liquid nature. On increasing the alcohol concentration up to 60 per cent. by volume, the gliadin will be maximally solvated, and will remain completely in solution, and will be insensible even to high concentrations of univalent electrolytes. In this medium, gliadin has obtained an albumin-like character. Whereas the concentrations of alcohol under 60 per cent. by volume increase the solvation of gliadin, higher concentrations have a desolvating influence. In consequence, starting from an uncharged gliadin sol in alcohol of 60 per cent., it is possible to realise all natures of sediments from liquid to solid.

In addition to the influence which change of medium exercises on the nature of the sediment, other physical conditions can have the same effect, *e.g.*, temperature and charge. Some proteins which normally flocculate can be made to separate at higher temperatures.

In the last few years these phenomena of separation have attracted the attention of several investigators. In particular, H. G. Bungenberg de Jong and H. R. Kruyt⁷ and their collaborators have investigated a large number of colloidal systems and in most cases they succeeded in producing separation phenomena.

We have discussed above the different factors influencing the phenomenon of separation, but even if the conditions are favourable, the question arises: How does this separation, this forming of drops, take place?

In our opinion the essential factors are not only the degree of solvation of the particles, but also the surface tension of the particles with their layers.

We will first consider the solvation. As the drops are liquid, the solvation of the system must be somewhat high. As we have discussed at length the discharging of a colloid with a small hydration will result in flocculation. If, on the other hand, the solvation is too large, the discharging will not have any visible effect. In order to separate this last-mentioned sol, the addition of a desolvating agent is necessary.

As the phenomenon of micro- and macro-separation on the discharging of a charged colloidal gliadin solution is a continuous process (as has been pointed out), we must assume that, strictly speaking, such a sol of maximal solvation is already a separated system. From this, it must

⁷ H. G. Bungenberg de Jong und H. R. Kruyt, *Koll. Z.*, **50**, (1), 39, 1930.



FIG. 1.—Gliadin (K1) \times 360.

[See page 28



FIG. 2.—Glutenin (iso-electric) \times 200.

[See page 32.

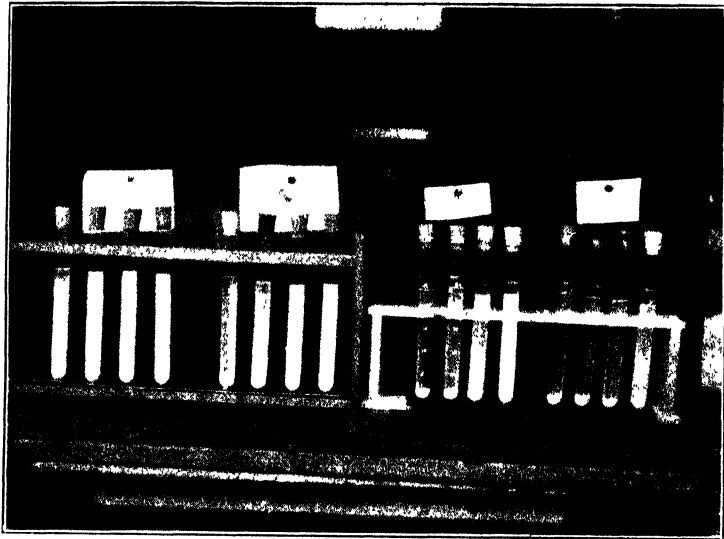


Fig. 5. -Influence of varying KI , KNO_3 , KBr and KCl concentration on an acid 80 per cent. acetone-glacial sol.
The concentration for every electrolyte decreases from left to right on the photo.

See page 41

follow that, even in a charged and solvated condition, a colloid particle surrounded by its solvation-layer has a definite surface tension towards the dispersion medium.

The surface tension, however, must be very small, and this for the following reasons. Firstly, a charged colloid particle has such a high solvation that a molecule on the outer sphere of the layer is only very weakly attracted towards the centre of the particle. Secondly, by charging a particle the surface tension is decreased. From this, it must follow that a decrease of the charge of solvated particles, will give an increase in the surface tension.

With regard to the enlarging of the drops by a decrease of charge, we can say that we have never observed any collision, and subsequent confluence of drops, so long as the protein is charged. The enlarging of the visible drops must, therefore, take place by collision with sub-microscopical protein particles. This phenomenon can be compared with the instability of highly-dispersed charged emulsions.

Influence of Electrolytes on Positive Gliadin Sols.

It is desirable briefly to pass in review the already known lyotropic phenomena of emulsoids. Considering the formula of Einstein-Smoluchowsky in its most simple form

$$\frac{\eta_s - \eta_0}{\eta_0} = k\phi(1 - f\zeta^2),$$

we observe that a decrease of the first term can be brought about either (a) as a result of a decrease of $f\zeta^2$, or (b) as a result of a diminution of ϕ .

When equivalent concentrations of electrolytes of the same valency are added, we observe a difference in the decrease in viscosity of protein solutions.

This can be explained by either (a) a decrease in viscosity caused by a decrease of charge (quasi-viscous effect), the same for all electrolytes of the same valency, or (b) a decrease in viscosity varying for electrolytes with the same valency (lyotropic influence).

So long as a colloid particle is charged, the added electrolyte molecules in the solution will direct their oppositely charged ions towards the charged particle. Therefore, in the case of the positive protein the principal lyotropic influence will be exerted by the negative ions.

For positive sols, the lyotropic series for the univalent negative ions in small concentrations runs as follows: SO_4 , F , Cl , Br , NO_3 , I , CNS , where CNS has the strongest influence on the dehydration of the particles and F exerts the least influence. In some special cases, however, Br and NO_3 can change their places in this series.

A similar series characteristic for the negative protein, is found with the positive ions, *viz.*, Li , Na , K , Rb , Cs . Here, too, some of the ions can interchange.

Although for the positive protein the principal lyotropic effect is defined by the negative ions, the positive ions will nevertheless exert a certain influence on the dehydration capacity of the negative ions. For this reason the lyotropic effect for NaCl and KCl in equivalent concentration cannot be the same.

We may assume that it is generally known that the lyotropic series occur not only in colloid-chemical phenomena, but that they can be found in several other physical processes. For instance, this series

appears in the change of the surface tension of water, in the decrease of solubility of organic substances by addition of electrolytes, etc.

The lyotropic series can be explained in several ways. Many investigators consider the degree of hydration of the different ions to be the cause of the differences in lyotropic effect.

The water binding capacity of different ions was determined by Remy, Washburn,⁸ and other investigators. Although the absolute values, determined by these workers, did not agree, nevertheless, generally speaking, the sequence of the water-binding capacity of the different ions was the same as in the lyotropic series, save for a few exceptions.

Robinson⁹ pointed out emphatically that a hydration layer is not a definite firm shell of molecules, but that the molecules in the outer sphere are less strongly orientated and are more or less movable. Consequently, there will be no hard and fast line between bound and unbound molecules. This must be the reason why different methods of determining the hydration give different results.

Other investigators sought a connection between the lyotropic effects and the difference in intensity of adsorption of the electrolytes. The following series was found by adsorption of electrolytes with the same cation on charcoal: CNS, I, Br, Cl, SO₄. This adsorption is probably very closely connected with the hydration, and very likely these effects are both expressions of the same specific property of the ion.

There remain to be mentioned the researches of Gortner, Sinclair and Hoffman¹⁰ carried out more particularly upon wheat proteins. These investigators experimented on the influence of higher electrolyte concentrations on the peptisation of the total proteins of wheat, and found a lyotropic series for the quantity of protein dissolved in different electrolyte solutions. This series was very marked for the negative ions, but for the positive ions it was less distinct; Na and K have changed places. Here (as always in higher electrolyte concentrations) the order of the lyotropic series is the reverse of that found in small electrolyte concentrations.

In an earlier paper¹ we published some viscosity determinations of the lyotropic influence of electrolytes on aqueous positive protein sols. In this case we found the usual order of the series Cl < Br < NO₃ < I < CNS. The SO₄, however, did not take its place. Evidently the discharging effect of the bivalent ion outbalances its lyotropic influence in small concentrations. Therefore it is impossible to get an impression of the lyotropic influence of this ion by comparing it with the univalent ions.

In the present paper we shall deal with the influence of electrolytes on the viscosity of gliadin sols, in alcohol and in acetone solutions. These investigations, carried out in various media, will give us a certain insight into the viscosity effects caused by the lyotropy and the charge of the ions. At the same time, they confirm the gradual nature of the separation phenomena and the increase in stability of the particles in definite alcohol- and acetone-water mixtures.

Alcohol Medium.

In an earlier publication² the influence of varying alcohol concentrations on the viscosity of a gliadin solution was studied. It was pointed

⁸ H. Remy, *Die electrolytische Wasserüberführung*, Berlin, 1927, Washburn, *J. Am. Chem. Soc.*, **31**, 322, 1909; *ibid.*, **37**, 674, 1915.

⁹ C. Robinson, *The Lyotropic Series*, Diss., Utrecht, 1929.

¹⁰ Gortner, Hoffman and Sinclair, *Colloid Symposium Mon.*, **5**, 179, 1927.

out that in 60 per cent. alcohol by volume the relative viscosity of these solutions passes through a maximum. This phenomenon exists in separated solutions as well as in clear solutions. At the same time, the influence of added acid on the percentage rise in viscosity was determined at this maximum. We concluded that the abnormally large percentage rise in viscosity in separated solutions was due to the dispersing action of alcohol on the agglomeration of particles.

This paper will deal with the influence of alcohol on gliadin solutions separated with different electrolytes and the following experiments will make it clear that in 48 per cent. alcohol by weight the colloid gliadin particle is in a special state.

(a) Firstly, we sought to ascertain whether the influence of different alcohol concentrations on an acid gliadin solution, separated with electrolytes, was analogous with the effects on separated solutions obtained by adding too small a quantity of acid for total peptisation.

The method of preparation of the acid sol was the same as in the previous paper. Five c.c. of a gliadin sol, obtained by shaking 3 gr. gliadin with 104 c.c. H_2O and 6 c.c. $1/10 N$. HCl , were put into a volumetric flask of 50 c.c., containing varying quantities of alcohol and 2 c.c. $0.25 N$. KCl . Therefore these solutions contain 10 mil. mol. KCl per litre. After bringing the solution to $25^\circ C$., it was made up to the mark with a few drops of distilled water. After equilibrium had been reached, viscosimeter determinations were made, both on the alcoholic protein solutions and on the corresponding alcohol-water mixtures. From these readings was calculated the viscosity of the protein relative to the alcohol medium (η_{rel}). These values are found in Table I. (Fig. 3).

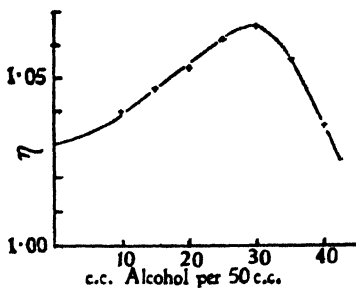


FIG. 3.—See Table I.
10 mil.-mol. KCl .

TABLE I.—INFLUENCE OF CHANGING ALCOHOL CONCENTRATION ON THE RELATIVE VISCOSITY OF AN ACID GLIADIN SOL WITH 10 MIL. MOL. KCl .*

0.	10.	15.	20.	25.	30.	35.	40.	45.	c.c. Alcohol.
—	1.855	2.325	2.718	2.949	3.021	2.913	2.644	—	η_{s+a}
—	1.784	2.233	2.583	2.780	2.838	2.760	2.555	2.245	η_a
1.030	1.039	1.046	1.052	1.061	1.065	1.055	1.035	—	$\frac{\eta_{s+a}}{\eta_a}$
—	30	53	73	103	117	83	17	—	rise per cent.
	<i>v. sl. cld.</i>	<i>sl. op.</i>	<i>clr.</i>	<i>clr.</i>	<i>clr.</i>	<i>sl. op.</i>	<i>sl. cld.</i>	<i>floc.</i>	appearance

* *v.* = very; *sl.* = slightly; *op.* = opalescent; *cld.* = cloudy; *clr.* = clear; *floc.* = flocculated.

The appearance of the solution, separated by electrolytes, changes with increasing alcohol concentration. Whilst the aqueous gliadin solution, containing 10 mil. mol. KCl , is cloudy, this turbidity disappears by adding alcohol, and on reaching a concentration of 30 to 40 per cent. alcohol by volume, the protein solution becomes water-clear. It remains so till about 70 per cent. alcohol by volume.

At alcohol concentrations of more than 70 per cent. by volume the protein solution becomes again opalescent, and afterwards cloudy, whereas at a concentration of 80 to 90 per cent. alcohol flocculation results. These phenomena are perfectly in accordance with the explanation given in a previous paper, *i.e.*, the alcohol at first exercises a dispersing effect caused by the enlarging of the protecting layer. Coupled with this is a stabilising effect.

In higher alcohol concentrations the gliadin loses one of its stability factors, and passes in a suspensoid. By the influence of the electrolyte in solution, discharging takes place and flocculation results. The curve obtained from the data of Table I. appears to have the same shape as that for a sol without electrolyte. The maxima in both these curves are found at the same alcohol concentration. The percentage rise in viscosity at the maximum $\frac{\eta_{rel.} - \eta_s}{\eta_s - 1}$ has a very large value because the aqueous solution was separated, just as in the case of sols, separated by a quantity of acid too small for complete peptisation.

(b) In addition, an investigation was carried out upon the change of the percentage rise in viscosity in 60 per cent. alcohol by volume

TABLE II.—INFLUENCE OF CHANGING ELECTROLYTE CONCENTRATION ON THE RELATIVE VISCOSITY OF AN ACID GLIADIN SOL IN WATER AND IN ALCOHOL 60 PER CENT. BY VOLUME.

0.4.	0.8.	2.	4.	6.	8.	Mil. Mol. KI Per Litre.
1.087	1.071	1.053	1.036	1.029	1.024	η_s
3.184	3.150	3.102	3.057	3.048	3.037	η_{s+a}
1.124	1.112	1.095	1.079	1.076	1.072	$\frac{\eta_{s+a}}{\eta_s}$
42	57	79	119	162	200	rise per cent.
<i>clr.</i>	<i>clr.</i>	<i>sl. op.</i>	<i>op.</i>	<i>cl.d.</i>	<i>cl.d.</i>	appearance of hydrosol

(at the maximum) with different quantities of electrolyte added. For this purpose 2.5 c.c. of a protein sol with varying quantities of KI and 15 c.c. alcohol were diluted in a volumetric flask to 25 c.c. in a thermostat at 25° C. After standing one hour, the viscosity readings were made. The final concentrations of KI in solution are 0.4, 0.8, 2, 4, 6 and 8 mil. mol. per litre. Table II. gives the results of the measurements.

It is evident that with increasing separation by addition of more electrolyte, the percentage rise in viscosity increases. Since the shape of the curve (obtained by plotting the values of the percentage rises in viscosity in 60 per cent. alcohol by volume against the viscosities of the corresponding hydrosols) is perfectly regular, it follows that the separation is a continuous process, and does not occur suddenly at a critical charge of the particles. This is in accordance with the previous measurements carried out with separated solutions obtained by peptisizing with too small a quantity of acid.

(c) In order to investigate the influence of alcohol on the lyotropic effect of different monovalent electrolytes, the following experiment was done :—

In a volumetric flask of 12.5 c.c. capacity, 1 c.c. of 0.15 N KCl or KI was added to 10 c.c. of a gliadin sol containing respectively 0, 20, 35

and 45 c.c. alcohol per 50 c.c. liquid. After making up to the mark at 25° C. with distilled water, the viscosities of these solutions were determined, as well as those of the corresponding alcohol-gliadin solutions without electrolyte and of the corresponding alcohol-water mixtures.

The relative viscosities $\frac{\eta_{s+A}}{\eta_A}$ of these three sols (KCl, KI and without electrolyte) in these different alcohol media were then calculated by dividing the viscosities of the alcohol sols by the corresponding viscosities of the alcohol-water mixtures. By interpolation from an alcohol-water viscosity graph, these alcohol-water mixtures were found to contain approximately 0, 26, 50, and 65 per cent. alcohol by weight. Table III. gives the results of these measurements.

TABLE III.—INFLUENCE OF DIFFERENT UNIVALENT NEGATIVE IONS ON THE RELATIVE VISCOSITY OF AN ACID GLIADIN SOL WITH VARYING ALCOHOL CONCENTRATION.

	0.	26.	50.	65.	Per Cent. Alcohol by Weight.
KCl	1'088	2'640	3'164	2'897	} η_{s+a}
KI	1'030	2'495	3'000	2'761	
	1'009	2'470	2'996	2'757	
	1'000	2'396	2'833	2'633	} η_a
KCl	1'088	1'102	1'117	1'101	} $\frac{\eta_{s+a}}{\eta_a}$
KI	1'030	1'041	1'059	1'049	
	1'009	1'031	1'058	1'048	
KCl	—	36'6	96'6	63'3	} rise per cent.
KI	—	244'	544'	433'	

These data indicate: (1) Two gliadin solutions with the same charge on the particles have a different percentage rise in viscosity when the same quantity of alcohol is added to both. (2) The percentage rise in viscosity by adding the same quantity of alcohol is larger for an electrolyte with a strongly dehydrating ion (lyotropic ion) than for one containing a less strong ion. (3) By increasing the alcohol concentrations till about 50 per cent., the relative viscosities of the gliadin-KCl sol and KI sol come up to each other. (4) In a medium of alcohol about 50 per cent. by weight the viscosities of the KCl and KI sol coincide within the experimental error. (5) This phenomenon takes place in the same alcohol concentration, wherein the gliadin alcohol sol without electrolyte has its maximum of viscosity.

It does not follow that protein solutions of the same concentration, with the same viscosity in water, will show the same percentage rise in viscosity in 60 per cent. alcohol by volume. We may consider two aqueous solutions of the same protein concentration with the same viscosity, the first solution obtained by adding a certain quantity of KCl, the second one by adding a different quantity of KI. The colloid particles in these solutions do not possess the same charge, for in aqueous medium the decrease in viscosity by adding electrolytes to most

emulsoids is not only the result of the discharging effects of the ion, but a second factor, the lyotropy, plays a leading part.

As the decrease in viscosity, due to the lyotropic effect of the ion, is less for the Cl ion than for the I ion, at least for positive sols, and with small electrolyte concentrations, a larger quantity of KCl than of KI must be added to the same protein solution to get the same lowering in viscosity. Therefore in the system KCl-gliadin the particles are less charged than in the system KI-gliadin.

On adding alcohol to these two solutions, the separated particles will be completely dispersed and clear solutions will result. The viscosities of these alcoholic solutions must be different, because the charge and the solvation of the particles are different. Consequently the percentage rises in viscosity for these KCl and KI gliadin solutions must be different in a medium of the same alcohol percentage. On the other hand, it is to be expected that solutions separated with equivalent quantities of KCl and KI (*i.e.*, solutions in which the particles have the same charge, but different solvation) will also show different percentage rises in viscosity in a medium of the same alcohol concentration. This is in accordance with the experimental facts of Table III.

(d) We next sought to ascertain whether the phenomena found with KCl and KI in a concentration of 12 mil. mol. in 50 per cent. alcohol by weight, were the same with all concentrations of these electrolytes, provided that the electrolytes were equimolar in solution. Table IV. gives viscosity measurements carried out upon an acid gliadin sol in 50 per cent. alcohol by weight by adding to this sol 0.8, 2 and 6 mil. mol. KCl and KI.

TABLE IV.—INFLUENCE OF CHANGING CONCENTRATION OF KCl AND KI ON THE RELATIVE VISCOSITY OF AN ACID GLIADIN SOL IN ALCOHOL 48 PER CENT. BY WEIGHT.

	0.8.	2.	6.	Mil. Mol. Electrolyte.
KCl	1.076	1.062	1.045	} η_s
KI	1.071	1.053	1.029	
KCl	3.147	3.102	3.050	} η_{s+a}
KI	3.150	3.102	3.048	
KCl	1.111	1.095	1.077	} $\frac{\eta_{s+a}}{\eta_a}$
KI	1.112	1.095	1.076	

From these data it is evident that the effects found in 50 per cent. alcohol by weight are independent of the electrolyte concentration, except that by increasing the concentration of electrolyte, the viscosity of the gliadin sol in 50 per cent. alcohol by weight decreases.

Summing up our investigations, we can say that in about 50 per cent. alcohol by weight, the effects of KI and KCl on the positive gliadin particle are the same. Before discussing these measurements, the figures of the measurements in acetone medium will be given, in order to have more facts at our disposal.

Acetone Medium.

A large number of measurements were carried out in varying acetone-water media, and with different uni- and divalent electrolytes. This medium was preferred to the alcoholic medium, because the latter must be absolutely free from oxidising agents to get accurate determinations. Traces of free iodine—caused by the oxidising actions of impurities in the alcohol on KI—have a marked lowering influence on the viscosities of gliadin sols. Acetone was free from these substances. A pure preparation was used, which was, moreover, rectified at its boiling-point.

The investigations in acetone media can be divided into three sections : (1) The influence of acetone on acid gliadin sols in the presence of different univalent electrolytes (*i.e.*, negative ions). (2) The influence of acetone on acid gliadin sols in the presence of di or polyvalent electrolytes. (3) The influence of changing p_H on the effects mentioned under the first and second sections. (4) The phenomena mentioned under sections 1 and 3 for higher protein concentrations.

For the determinations in this part of the paper the electrolytes were added only in very small concentrations. The influence of higher electrolyte concentrations will be dealt with separately.

1. Univalent Electrolytes.

From the previously mentioned analogous behaviour of acid gliadin sols in alcohol and acetone media without electrolytes, it was to be expected that the effects of electrolytes on sols in acetone would be analogous to those in alcohol. This was actually the case.

Aqueous sols separated by addition of electrolytes, became water-clear again when acetone was added. In higher acetone concentrations for a second time a turbidity of the sol appears. If a sufficient quantity of electrolyte is added, and the acetone concentration in the sol is high enough, flocculation results, owing to the discharging of the practically desolvated particle. If the concentration of acetone in the sol is too low, but if there is a sufficient quantity of electrolyte, there results, on the other hand, sediments, which (microscopically observed) are intermediate between separation and flocculation. Relative viscosity curves, from the figures in the following tables, were obtained by varying the acetone concentration in a gliadin sol separated by electrolytes; these curves had a form analogous with that of a sol without electrolyte. The maximum in the relative viscosity curve was found at the same acetone concentration, with or without electrolytes. It was found that the relative viscosities of gliadin sols with equivalent concentrations of KCl and KI approached one another with increasing acetone concentration. In acetone 44 per cent. by volume (at the maximum) the relative viscosities of the sols were identical. At higher acetone concentrations the relative viscosity curves separate again. We shall refer to this later. Table V. (Fig. 4)

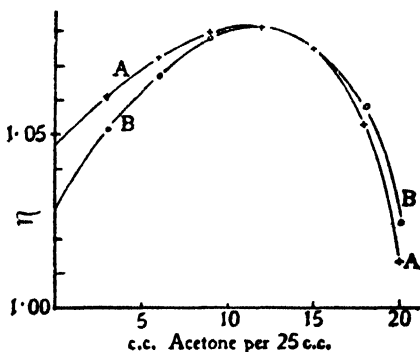


FIG. 4. —See Table V.
Curve A = KCl
B = KJ.

gives a series of measurements carried out on sols containing 4 mil. mol. KI and KCl, and varying acetone concentration.

The purpose of the following experiments was to determine whether this coincidence of the relative viscosities of gliadin sols with 4 mil. mol. KI and KCl in acetone of about 44 per cent. was the case for all concentrations of these electrolytes.

TABLE V.—INFLUENCE OF VARYING ACETONE CONCENTRATION ON THE RELATIVE VISCOSITY OF GLIADIN SOLS WITH 4 MIL. MOL. KCl AND KI.

	0.	3.	6.	9.	12.	15.	18.	20.	c.c. Acetone.
KCl {	1'233	1'443	1'579	1'600	1'479	1'221	0'987		η_{ac}
	1'308	1'547	1'705	1'730	1'590	1'286	1'005		η_{s+ac}
	1'047	1'061	1'072	1'079	1'081	1'075	1'053	1'013	$\frac{\eta_{s+ac}}{\eta_{ac}}$
		<i>sl. op.</i>						<i>cl. flocc.</i>	appearance
KI {	1'298	1'540	1'702	1'729	1'591	1'292	1'016		η_{s+ac}
	1'029	1'053	1'067	1'078	1'081	1'075	1'058	1'024	$\frac{\eta_{s+ac}}{\eta_{ac}}$
		<i>sl. op.</i>						<i>op.</i>	appearance

For this purpose 12 c.c. acetone, different equivalent quantities of KI and KCl and 2.5 c.c. of an acid gliadin sol were put into volumetric flasks of 25 c.c. capacity. After making up to the mark at 25° C., the final concentrations of the electrolytes were respectively 0, 2, 4, 6, 8, 10, 12, 14, 20, 28, and 40 mil. mol. per litre. At the same time the

TABLE VI.—INFLUENCE OF VARYING CONCENTRATIONS OF KI AND KCl ON THE RELATIVE VISCOSITY OF AN ACID 44 PER CENT. ACETONE GLIADIN SOL.

Mil. Mol.	0.	2.	4.	6.	8.	10.	12.	20.	28.	40.	80.
$\eta_{s+Ac} + KCl$	1805	1737	1722	1716	1713	1703	1702	1697	1692	1695	1694
$\eta_{Ac+w} + KCl$	1602	—	—	—	—	—	1605	1600	1597	1601	1602
$\eta_{s+Ac} + KI$	1805	1742	1722	1714	1711	1702	1698	1694	1688	1685	1677
$\eta_{Ac+w} + KI$	1602	—	—	—	—	—	1600	1597	1593	1594	1587
$\frac{\eta_{s+Ac} + KI}{\eta_{Ac}}$ I	1127	1088	1075	1070	1069	1063	1062	1061	1060	1057	1057
$\frac{\eta_{s+Ac} + KCl}{\eta_{Ac}}$ II	1127	1086	1075	1071	1070	1064	1061	1060	1060	1059	1058

corresponding acetone-water-electrolyte mixtures were made. The viscosity determinations were carried out upon sols which had been left for twelve hours. Table VI. gives the results of these measurements. If we examine these data, the following facts can be observed: (a) The relative viscosities of sols with equivalent concentrations of KI and KCl are the same within experimental error in about 44 per cent. acetone

medium. (b) By increasing the electrolytic concentration in the sols a gradual decrease in the relative viscosity takes place.

In acetone concentrations of more than 44 per cent. by volume, the viscosity curves of KI and KCl separate again (see Table VI.). In order to get a clearer insight into this phenomenon, the influence of other monovalent ions on an acid gliadin solution in higher acetone concentrations was studied. For this purpose, 20 c.c. acetone and 3.5 c.c. of electrolyte solutions of varying concentration were added to 2 c.c. of an acid aqueous gliadin sol in steamed flocculation tubes, so that the final concentrations of the used electrolytes were respectively 4, 5, 6 and 7 mil. mol., and the final acetone concentration was about 80 per cent. by volume. The electrolytes used were KCl, KBr, KNO_3 and KI. The appearance of the liquids in the tubes shows at once that the same concentrations of

TABLE VII.—INFLUENCE OF VARYING CONCENTRATIONS OF DIFFERENT UNIVALENT ELECTROLYTES ON A GLIADIN SOL OF 80 PER CENT. \pm ACETONE BY VOLUME.

Mil. Mol.	4.	5.	6.	7.	
KI {	slightly opalescent	opalescent	slightly cloudy	cloudy	after 1 hr.
	cloudy	cloudy	cloudy	cloudy trace sediment	after 36 hrs.
KNO_3 {	opalescent	slightly cloudy	cloudy	cloudy	after 1 hr.
	slightly cloudy	slightly cloudy trace sediment	slightly cloudy sediment	opalescent sediment	after 36 hrs.
KBr {	slightly cloudy	cloudy	cloudy	cloudy	after 1 hr.
	slightly cloudy trace sediment	slightly cloudy sediment	opalescent sediment	clear sediment	after 36 hrs.
KCl {	very cloudy	very cloudy	very cloudy	very cloudy	after 1 hr.
	slightly cloudy sediment	opalescent sediment	clear sediment	clear sediment	after 36 hrs.

different univalent electrolytes in this acetone medium have different influences on the partly desolvated gliadin; *e.g.*, after thirty-six hours a slight trace of sediment appeared on the bottom of the tube containing the highest KI concentration (7 mil. mol.), while the tubes containing respectively 6, 5 and 4 mil. mol. were only turbid. On the other hand, with a KCl concentration of 4 mil. mol. the protein has practically settled down, and with higher KCl concentrations the supernating liquid was practically clear. KNO_3 and KBr were found to be between these two extremes.

Fig. 5 shows the different influences of the monovalent ions in acetone of about 80 per cent. From this we may conclude that in higher acetone concentrations the lyotropic influence of the ions reappears, but in a series reversed from that in aqueous medium. In other words, in higher acetone concentrations KCl has the strongest desolvating influence on the

particle, while KI influences the solvation of the particles least. In the last section of this paper we shall deal with this phenomenon; for the present, it suffices to say that in acid gliadin solutions the lyotropic series of the monovalent ions is dependent on the nature of the medium.

We thought it desirable more closely to study viscosimetrically the influence of the other monovalent electrolytes on an acid gliadin sol in varying acetone media. As the relative viscosity curves with varying acetone concentration of a KI and KCl gliadin sol intersect in acetone of about 44 per cent. by volume, there were two possible ways in which the other monovalent electrolytes might behave: (1) The respective viscosity curves of a gliadin sol, with the same concentration of monovalent electrolytes in varying acetone medium, might run through the same point of intersection (*i.e.*, about 44 per cent. acetone); (2) the respective viscosity curves might intersect at different acetone concentrations. If we found that the respective viscosity curves of a gliadin sol with the same concentration of KCl, KBr, KNO_3 , KI and KCNS ions meet at a point corresponding to the same percentage of acetone (in other words, in a special acetone concentration (44 per cent. \pm acetone) the relative viscosity is independent of the nature of the monovalent electrolyte, and we should have thus an indication that the important criterion is not the structure of the ion, but only the state of the protein particle in this medium.

However, if we found that the respective viscosity curves of a gliadin sol with different monovalent ions intersect at different concentration of acetone, such a deviation should be markedly found for KCNS and KNO_3 , because of the complex nature of the negative ions. In the case of KBr, the properties of which stand between KCl and KI, a big deviation from the behaviour of KCl and KI was not to be expected.

In order to investigate these possibilities, the following experiments were carried out. To 2.5 c.c. of an acid gliadin sol in several volumetric flasks of 25 c.c. that quantity of electrolyte was added which was necessary to ensure that the final concentration was 6 mil. mol., after adding respectively 0, 3, 6, 10, 12, 15 and 18 c.c. acetone, and making up to the mark with distilled water. At the same time the corresponding acetone gliadin sols without electrolyte were made. The electrolytes used were KCl, KBr, KI, KNO_3 and KCNS. At the same time, we sought to ascertain whether an organic electrolyte sodium sulphomethane* ($\text{CH}_3 \cdot \text{SO}_3\text{Na}$) fitted in the same series. The viscosities of the aqueous solutions were determined immediately after the solutions were made up, those of the acetone sols after twenty-four hours. The viscosities of the gliadin sols with the same acetone concentration, though with different electrolytes, were measured in the same viscosimeters.

Table VIII. gives the data of these measurements.

We may conclude from this:

(1) With increasing acetone concentration, the relative viscosities of the sols, with the same quantity of different univalent electrolyte, increase and approach each other.

(2) In acetone concentration under 44 per cent., the lyotropic series remains the same as in the aqueous medium ($\text{CNS} > \text{I} > \text{NO}_3 > \text{Br} > \text{Cl}$).

(3) Within experimental error, the relative viscosity of a sol in 44 per cent. acetone is independent of the nature of the added univalent electrolyte, provided that the concentration is the same.

* We are indebted to Prof. Backer of the University of Groningen, who provided us with this and other substituted methane preparations.

(4) In acetone of a concentration of about 44 per cent. by volume, the relative viscosity curves intersect.

(5) In acetone concentration of more than 44 per cent. the respective viscosity curves separate.

TABLE VIII.—INFLUENCE OF VARYING ACETONE CONCENTRATION ON THE RELATIVE VISCOSITY OF ACID GLIADIN SOLS WITH 6 MIL. MOL. OF DIFFERENT UNIVALENT ELECTROLYTES.

	a.	3.	6.	10.	12.	15.	18.	cc. Acetone.
Without Electrolyte {	— 1'090	1'359 1'102	1'616 1'120	— —	1'823 1'140	— —	1'351 1'106	$\frac{\eta_s+ac}{\eta_s+ac}$ η_{ac}
CH ₃ SO ₃ Na {	— 1'040	1'304 1'057	1'539 1'067	— —	1'719 1'074	— —	1'282 1'050	$\frac{\eta_s+ac}{\eta_s+ac}$ η_{ac}
KCl {	— 1'036	1'299 1'053	1'538 1'066	1'716 1'073	1'719 1'074	1'582 1'069	1'274 1'044	$\frac{\eta_s+ac}{\eta_s+ac}$ η_{ac}
KBr {	— 1'032	1'293 1'049	1'535 1'064	1'716 1'073	1'717 1'073	1'582 1'069	— —	$\frac{\eta_s+ac}{\eta_s+ac}$ η_{ac}
KNO ₃ {	— 1'029	1'293 1'049	1'534 1'063	1'718 1'074	1'717 1'073	1'583 1'070	1'280 1'049	$\frac{\eta_s+ac}{\eta_s+ac}$ η_{ac}
KI {	— 1'018	— —	— —	— —	1'718 1'073	— —	1'282 1'050	$\frac{\eta_s+ac}{\eta_s+ac}$ η_{ac}
KCNS {	— 1'015	1'286 1'043	1'528 1'059	1'716 1'073	1'719 1'074	1'584 1'071	1'289 1'056	$\frac{\eta_s+ac}{\eta_s+ac}$ η_{ac}
	—	09108	15932	20404	20404	16994	08664	log η_a

(6) This second separation gives a lyotropic order the reverse of that shown in aqueous medium (Cl > Br > NO₃ > I > CNS).

(7) Sodium sulphomethane has a weaker lyotropic effect in aqueous medium than KCl, therefore it takes the place in the lyotropic series, which the SO₄²⁻-ion would occupy if it could act as a univalent instead of as a bivalent ion.

(8) In acetone concentration of more than 44 per cent. sodium sulphomethane behaves in an abnormal way. It was to be expected that it would have a desolvating effect stronger than KCl. It is possible that the anomaly in this organic medium is due to the organic character of the anion.

From a large number of viscosimetric determinations carried out on acid gliadin sols of practically the same H-ion concentration, and containing varying quantities of KCl and KI as well as of acetone, it was possible to construct the three-dimensional graph given in Fig. 6. On the axes are plotted the electrolyte concentration, the relative viscosity of the sols and the acetone concentration. In the interests of brevity,

we refrain from giving the data in a table.

As the sols were made on different days, slight fluctuations in the values used are possible. This is, however, not important, for our purpose was merely to get a general impression of the behaviour of gliadin in these media.

It is to be expected that while the viscosimetric curves, obtained by the addition of varying quantities of different electrolytes to different proteins will have the same shape in aqueous medium, this will probably not be the case in binary mixtures of solvents, so that possible differences between different

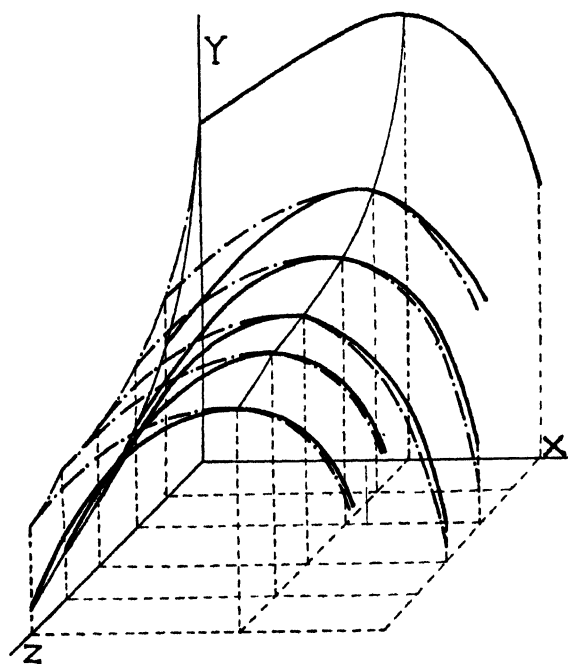


FIG. 6.

X Axis Concentration of acetone.
Y Axis Relative viscosity.
Z Axis Concentration of electrolyte.
— KI. — — KCl.

proteins will be emphasised under these circumstances.

From the graph obtained in this way, it appears that the shape of the curve of the relative viscosity plotted against the acetone concentration is not dependent upon the quantity of electrolyte added, *i.e.*, the charge of the sol. By increasing the electrolyte concentration, the curves merely lie on a lower level. The acetone concentration at which the maximum occurs does not change with the charge of the sol.

2. Polyvalent Ions.

In order to study the influence of bivalent ions the same method was followed as in the case of monovalent ions. Here, too, we studied the change in the relative viscosity of gliadin sols with a constant quantity of K_2SO_4 , but with varying acetone concentrations.

The shape of the curve was similar to that of gliadin sols with a univalent ion, with a maximum at an acetone concentration of about 44 per cent. At higher acetone concentrations flocculation occurs as a result of the discharging influence of the bivalent ion and of the partial desolvation of the gliadin particle. By comparing the curves of gliadin sols with equivalent concentration of KCl and K_2SO_4 , it appeared that the maximum in the relative viscosity curve for the sol containing sulphate was lower than that for the sol with KCl. This was to be expected, since the sulphate ion, being bivalent, has a stronger discharging influence.

We next investigated the influence of two different bivalent electrolytes, namely K_2SO_4 and $CH_3(SO_3K)_2$. When these electrolytes were added to aqueous gliadin sols, the viscosity determinations showed that the lyotropic influence is not the same. This difference is not so striking

TABLE IX.—INFLUENCE OF VARYING K_2SO_4 AND $CH_3(SO_3K)_2$ CONCENTRATION ON THE RELATIVE VISCOSITY OF A POSITIVE AQUEOUS AND 44 PER CENT. ACETONE GLIADIN SOL.

	0.	1.	2.	4.	6.	8.	Mil. eq.
K_2SO_4 {	1'089 —	1'043 <i>v. sl. op.</i>	1'033 <i>sl. cld.</i>	1'027 <i>sl. cld.</i>	1'022 <i>cld.</i>	1'018 <i>cld.</i>	$\eta_s + w$ appearance
$CH_3(SO_3K)_2$ {	1'089 —	1'035 <i>op.</i>	1'027 <i>sl. cld.</i>	1'021 <i>cld.</i>	1'017 <i>v. cld.</i>	— <i>flocc.</i>	$\eta_s + w$ appearance
K_2SO_4 {	1'824 1'140	1'711 1'070	1'699 1'062	1'697 1'060	1'691 1'057	1'691 1'057	$\frac{\eta_s + Ac}{\eta_{Ac}}$
$CH_3(SO_3K)_2$ {	1'824 1'140	1'772 1'071	1'701 1'063	1'695 1'060	1'693 1'058	1'692 1'058	$\frac{\eta_s + Ac}{\eta_{Ac}}$

as is found in the case of different univalent ions, though it is clearly perceptible. In aqueous media, $CH_3(SO_3K)_2$ has a stronger dehydrating influence than K_2SO_4 . The differences in viscosity in aqueous solutions found for equivalent concentration of these electrolytes disappear in 44 per cent. acetone. In this acetone medium the relative viscosities of gliadin sols with equivalent concentration of these two electrolytes, coincide within experimental error. Table IX. gives a review of viscosity data.

In higher acetone concentration the same phenomenon is displayed as in the case of univalent ions, namely, the reversal of the lyotropic series. As the lyotropic difference between the SO_4 ion and the $CH_3(SO_3)_2$ ion is very small, this reversal of the lyotropic series in higher acetone concentration is not so marked as for the univalent ions. It appeared that with gliadin solutions containing about 75 per cent. acetone, and respectively 2, 4, 6 and 8 mil. eq. of the afore-mentioned electrolytes, those

solutions containing 4, 6 and 8 mil. eq. of either electrolytes were completely flocculated after twelve hours. The solution containing 2 mil. eq. K_2SO_4 was only partly precipitated, while the solution of 2 mil. eq. $CH_2(SO_3K)_2$ was merely cloudy, and did not show any precipitate. Thus all the effects produced by addition of bivalent ions to a 44 per cent. acetone gliadin sol are the same as for the monovalent ions, except that the discharging effect is not the same.

We next studied the influence of tri- and tetra-valent ions on an acid gliadin sol of 44 per cent. acetone. The trivalent electrolyte used was $CH(SO_3K)_3$. As this substance is only slightly soluble in the acetone medium, it was only possible to reach a final concentration of 1 mil. eq. When more electrolyte was added, not only the salt, but part of the protein was precipitated (after the addition of acetone).

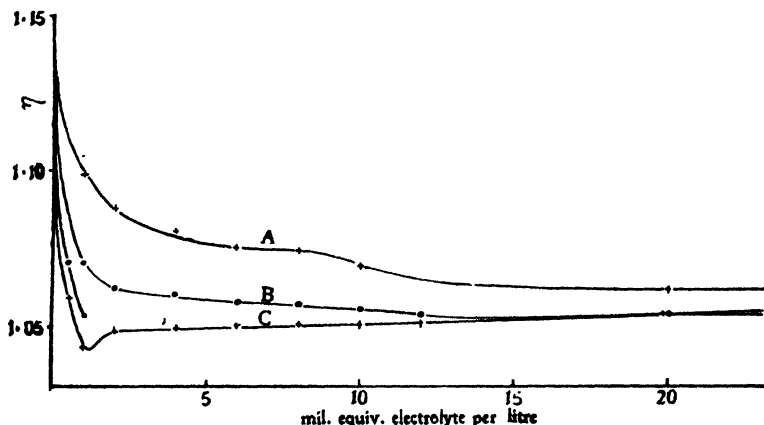


FIG. 7.—See Table X.
Curve A = KCl
" B = K_2SO_4
" C = $K_4Fe(CN)_6$.

By addition of $K_4Fe(CN)_6$ to acid 44 per cent. acetone gliadin sols, another phenomenon was observed. The first traces of $K_4Fe(CN)_6$ have no influence on the appearance of the solution, but there is a sharp drop in the viscosity. After this, at a concentration of $K_4Fe(CN)_6$ of about 1 to 4 mil. eq., the solutions are more or less cloudy. The viscosities of these solutions were determined after thirty minutes instead of twenty-four hours, because after a day the protein had settled down. By addition of more $K_4Fe(CN)_6$ the solutions are again absolutely clear, and there is a gradual small rise in viscosity.

Table X. gives the results (Fig. 7).

When the data of Table XI. for KCl, K_2SO_4 , $CH(SO_3K)_3$ and K_4FeCy_6 are plotted, we observe the following facts: (1) On discharging of acid 44 per cent. acetone gliadin sols there is a distinct divergence of the relative viscosity curves for ions of different valency; (2) the viscosities of sols discharged with ions of different valency do not reach the same level.

Influence of Changing H-Ion Concentration on 44 Per Cent. Acetone Gliadin Solutions containing Electrolyte.

The foregoing conclusions are valid only for an acid-acetone sol of maximal viscosity. In order to obtain a more complete insight into

the influence of electrolytes of different valency, it was thought desirable to study the effect at different p_H . With this end in view, the following questions were studied: (1) What is the effect of uni- and polyvalent ions on the relative viscosity of an uncharged 44 per cent. acetone gliadin sol? (2) What is the effect of changing p_H on the relative viscosity of a sol containing varying quantities of KCl? (3) What is the influence of changing p_H on the relative viscosity of a sol containing a definite quantity of uni- or polyvalent electrolyte? (In our experiments we used 10 mil. eq. of electrolytes because the viscosity of an acid sol practically did not decrease when still more KCl was added.)

For the experiments in this part the following method of preparing the sol was used. In a thermostat at 25° C. 1.3636 gr. gliadin was shaken with a mixture of acetone and water. This mixture was made at 25° C. by diluting 200 c.c. acetone with distilled water to 500 c.c. in a volumetric flask. The protein solution thus obtained was not filtered, in order to avoid evaporation of acetone, but was allowed to stand for thirty minutes so that small particles of filter paper could settle down. Two and a half cubic centimetres of this gliadin solution were pipetted into 25 c.c. volumetric flasks with 11 c.c. acetone and the necessary quantity of electrolyte, and made up to the mark at 25° C. The advantage of

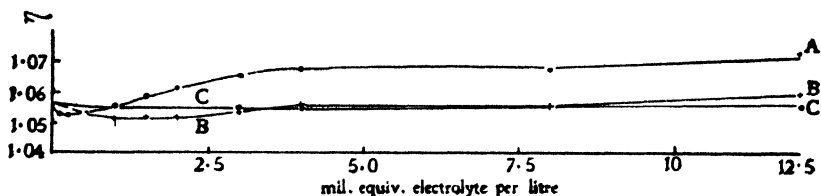


FIG. 8.—See Table XI.
Curve A = $K_4Fe(CN)_6$
" B = K_2SO_4
" C = KCl.

preparing the solutions by this method was that the protein as well as the acetone concentration (44 per cent.) were practically the same as in those used in our former experiments. Thus it is possible to compare these experiments with the previous measurements.

From the Table XI. (Fig. 8), it will be evident that addition of varying quantities of uni- and polyvalent electrolytes has wholly different effects on the relative viscosity of a practically uncharged gliadin sol. Practically no lowering in the relative viscosity of these sols took place by addition of varying quantities of KCl (1, 4, 8, 10 and 14 mil. eq.). The values of these measurements plotted against the KCl concentration give a horizontal line. On the other hand, the relative viscosity curve, obtained by addition of varying quantities of the bivalent K_2SO_4 , shows another shape.

The first additions of K_2SO_4 give a slight lowering in the relative viscosity, reaching a minimum at a concentration of about 1.5 mil. eq. By further increasing the K_2SO_4 concentration, the relative viscosity rises gradually even above its initial value. With $K_4Fe(CN)_6$ the same phenomenon (but even more pronounced) can be observed. Very small quantities cause a decrease in the relative viscosity. The minimum in the relative viscosity is found at a concentration of about 0.25 mil. eq. By increasing the $K_4Fe(CN)_6$ concentration a rise in the relative

TABLE X.—INFLUENCE OF CONCENTRATIONS OF DIFFERENT VALENT ELECTROLYTES ON THE RELATIVE VISCOSITY OF AN ACID 44 PER CENT. ACETONE GLIADIN WITH MAXIMAL VISCOSITY.

a.	b.	1.	2.	4.	6.	8.	10.	12.	16.	20.	30.	36.	Mil. Eq. Electrolytes. $\frac{\eta_s + Ac}{\eta_s + Ac + \eta_{Ac+electr.}}$
KCl	1'824	1'758	1'740	1'727	1'720	1'718	1'711	—	—	1'702	1'701	—	$\frac{\eta_s + Ac}{\eta_s + Ac + \eta_{Ac+electr.}}$
	1'140	1'099	1'088	1'080	1'075	1'074	1'069	—	—	1'061	1'061	—	
K_2SO_4	1'824	1'711	1'699	1'697	1'692	1'691	1'686	1'688	—	1'689	1'695	1'697	$\frac{\eta_s + Ac}{\eta_s + Ac + \eta_{Ac+electr.}}$
	1'140	1'070	1'062	1'060	1'057	1'057	1'055	1'053	—	1'053	1'053	1'051	
$CH(SO_3K)_3$	1'824	1'685	—	—	—	—	—	—	—	—	—	—	$\frac{\eta_s + Ac}{\eta_s + Ac + \eta_{Ac+electr.}}$
	1'140	1'053	—	—	—	—	—	—	—	—	—	—	
$K_4Fe(CN)_6$	1'824	1'694	1'669	1'677	1'678	1'680	1'681	1'684	1'690	1'691	1'701	1'703	$\frac{\eta_s + Ac}{\eta_s + Ac + \eta_{Ac+electr.}}$
	1'140	1'059	1'043 <i>cl.</i>	1'018 <i>v. cl.</i>	1'019 <i>sl. cl.</i>	1'050	1'051	1'051	1'052	1'054	1'053	1'055	

viscosity occurs, and this reaches a value distinctly above the relative viscosity of the sol without electrolyte at a concentration of 3 mil. eq.

We may conclude from these experiments that the minimum in relative viscosity shifts with the valency of the negative ion. The higher the valency, the lower will be the concentration of electrolyte at the minimum, and the sharper will be the rise in relative viscosity afterwards by adding more electrolyte.

We next investigated the influence of changing H-ion concentration on an acetone gliadin sol with varying quantities of KCl. Table XII. gives a series of measurements, showing the final concentration of electrolyte and acid in the sols. It will be apparent, (1) that with increasing charge of the gliadin sol, the discharging effect of KCl will be more prominent, (2) that the level of the relative viscosity (obtained by discharging different charged sol with 10 to 14 mil. eq. KCl) rises with increasing charge of the initial sol, (3) that this rise in level does not stop at that p_H at which a sol without electrolyte has its

TABLE XI.—INFLUENCE OF VARYING EQUIVALENT CONCENTRATIONS OF KCl, K_2SO_4 , AND $K_4Fe(CN)_6$ ON THE RELATIVE VISCOSITY OF A GLIADIN SOL WITHOUT ACID IN ACETONE 44 PER CENT. BY WEIGHT.

	0.	0.125.	0.25.	0.5.	1.	1.5.	2.	3.	4.	8.	12.	Mil. Eq. Electr. per Litre.
KCl	1.690	—	—	—	1.689	—	—	1.687	1.688	1.689	1.689	$\frac{\eta_s + Ac}{\eta_{Ac}}$
	1.057	—	—	—	1.056	—	—	1.055	1.055	1.056	1.056	$\frac{\eta_s + Ac}{\eta_{Ac}}$
K_2SO_4	1.690	—	1.688	1.686	1.683	1.683	1.683	1.686	1.689	1.690	1.695	$\frac{\eta_s + Ac}{\eta_{Ac}}$
	1.057	—	1.055	1.054	1.052	1.052	1.052	1.054	1.056	1.056	1.060	$\frac{\eta_s + Ac}{\eta_{Ac}}$
$K_4Fe(CN)_6$	1.690	1.684	1.684	1.686	1.689	1.694	1.699	1.705	1.708	1.708	1.717	$\frac{\eta_s + Ac}{\eta_{Ac}}$
	1.057	1.053	1.053	1.054	1.056	1.059	1.062	1.066	1.068	1.068	1.073	$\frac{\eta_s + Ac}{\eta_{Ac}}$

TABLE XII.—INFLUENCE OF CHANGING ACID CONCENTRATION ON THE RELATIVE VISCOSITY OF A GLIADIN SOL WITH VARYING KCl CONCENTRATION IN ACETONE 44 PER CENT. BY WEIGHT.

Mil. Eq. HCl Per Litre.	0.	3.	6.	8.	10.	14.	Mil. Eq. Electr. per Litre.
0	1.689	1.687	1.688	1.688	1.692	1.689	$\frac{\eta_s + Ac}{\eta_{Ac}}$
	1.056	1.055	1.056	1.055	1.058	1.056	$\frac{\eta_s + Ac}{\eta_{Ac}}$
0.2	1.730	1.699	1.697	1.692	1.692	1.692	$\frac{\eta_s + Ac}{\eta_{Ac}}$
	1.081	1.062	1.061	1.058	1.058	1.058	$\frac{\eta_s + Ac}{\eta_{Ac}}$
0.4	1.775	1.713	1.705	1.705	1.704	1.701	$\frac{\eta_s + Ac}{\eta_{Ac}}$
	1.110	1.071	1.066	1.065	1.065	1.063	$\frac{\eta_s + Ac}{\eta_{Ac}}$
0.6	1.812	1.724	1.714	1.712	1.709	1.703	$\frac{\eta_s + Ac}{\eta_{Ac}}$
	1.113	1.077	1.072	1.070	1.068	1.065	$\frac{\eta_s + Ac}{\eta_{Ac}}$
0.8	1.826	1.727	1.718	1.715	1.710	1.710	$\frac{\eta_s + Ac}{\eta_{Ac}}$
	1.141	1.080	1.074	1.072	1.069	1.069	$\frac{\eta_s + Ac}{\eta_{Ac}}$
1.2	1.808	1.740	1.726	1.723	1.718	1.716	$\frac{\eta_s + Ac}{\eta_{Ac}}$
	1.130	1.088	1.079	1.077	1.074	1.073	$\frac{\eta_s + Ac}{\eta_{Ac}}$
1.6	1.794	1.735	1.728	—	1.717	1.715	$\frac{\eta_s + Ac}{\eta_{Ac}}$
	1.122	1.085	1.080	—	1.074	1.072	$\frac{\eta_s + Ac}{\eta_{Ac}}$
4.0	1.748	1.727	1.718	—	—	1.712	$\frac{\eta_s + Ac}{\eta_{Ac}}$
	1.092	1.080	1.074	—	—	1.070	$\frac{\eta_s + Ac}{\eta_{Ac}}$

maximal viscosity, but that its highest value is reached at a slightly higher H-ion concentration; in other words, the relative viscosity maxima of a sol with and without electrolyte are found at different H-ion concentrations.

By increasing the acid concentration of a sol beyond its viscosity maximum, the discharging effect of the Cl^- ions will cause a decrease in viscosity. Therefore, addition of KCl as a discharging agent will have a smaller effect because of the smaller charge of the particles in the sol. At length, a H-ion concentration will be reached at which addition of KCl will have practically no effect on the relative viscosity of the sol, in which case the relative viscosity curve will be practically a horizontal line, but at a level considerably higher than that of the sol without acid and varying quantities of KCl .

We may now discuss briefly the influence of varying H-ion concentrations on 44 per cent. acetone gliadin sols with and without 10 mil. eq. KCl , K_2SO_4 and K_4FeCy_6 (Table XIII.) (Fig. 9).

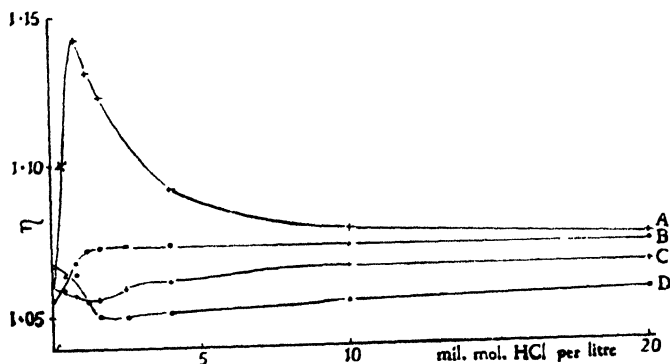


FIG. 9.—See Table XIII.
Curve A = Without electrolyte
" B = KCl
" C = K_2SO_4
" D = $\text{K}_4\text{Fe(CN)}_6$.

It is evident that increase of the H-ion concentration of a sol containing 10 mil. eq. KCl gives, at first, an increase in the relative viscosity until at a concentration of about 1.2 mil. eq. HCl the relative viscosity becomes practically independent of further increase of acidity in the sol. As was to be expected, the maximal relative viscosities of a sol with and without 10 mil. eq. KCl are found at different acid concentrations. Changing the p_{H} of sols containing 10 mil. eq. K_2SO_4 gives a completely different effect. The initial small additions of acid cause a lowering in the relative viscosity. A minimum is reached at about 1.2 to 1.6 mil. eq. HCl . By further increasing the acid concentration the relative viscosity curve rises again, to reach a value of 8 units above the initial viscosity, at an acid concentration of 20 mil. eq. HCl .

By changing the p_{H} of sols containing 10 mil. eq. $\text{K}_4\text{Fe(CN)}_6$ an analogous effect occurs, except that whereas the sols with 10 mil. eq. K_2SO_4 are all perfectly clear at the acid concentrations used, those containing 10 mil. eq. $\text{K}_4\text{Fe(CN)}_6$ are not clear. The first traces of acid alter the appearance of the originally clear sol, but by adding 1.6 to 4 mil. eq. HCl the sols become more or less cloudy, and in some cases part of

the protein settles down after twenty-four hours. (The viscosities of these cloudy solutions were determined after one hour instead of after twenty-four hours.)

Here we have a separation phenomenon in 44 per cent. acetone sol, probably caused by the discharging effect of a polyvalent complex ion. The sediment, when examined under the microscope, showed a number of small drops.

By further increasing the acid concentration the sols become perfectly clear again. Coincident with these phenomenon there is a change in the intensity of the yellow colour of the sols.

TABLE XIII.—INFLUENCE OF CHANGING HCl CONCENTRATION ON THE RELATIVE VISCOSITY OF GLIADIN SOLS WITH 10 M. EQ. KCl, K_2SO_4 AND K_4FeCy_6 IN ACETONE 44 PER CENT. BY WEIGHT.

	0.	0.4.	0.8.	1.2.	1.6.	2.5	4.	10.	20.	Mil. Eq. HCl Per Litre.
Wi hout electrolyte {	1.690	1.812	1.826	1.808	1.794	—	1.748	1.724	1.718	$\frac{\eta_{s+ac}}{\eta_{ac}}$
	1.056	1.110	1.141	1.130	1.122	—	1.092	1.078	1.074	$\frac{\eta_{s+ac}}{\eta_{ac}}$
10 m. eq. KCl {	1.689	1.694	1.708	1.714	1.715	1.716	1.716	1.714	1.714	$\frac{\eta_{s+ac}}{\eta_{ac}}$
	1.056	1.059	1.068	1.072	1.072	1.073	1.073	1.072	1.072	$\frac{\eta_{s+ac}}{\eta_{ac}}$
10 m. eq. K_2SO_4 {	1.695	1.694	1.691	1.689	1.689	1.694	1.696	1.705	1.703	$\frac{\eta_{s+ac}}{\eta_{ac}}$
	1.060	1.059	1.057	1.056	1.056	1.059	1.061	1.066	1.065	$\frac{\eta_{s+ac}}{\eta_{ac}}$
10 m. eq. K_4FeCy_6 {	1.706	1.702	1.702	1.687	1.679	1.680	1.682	1.685	1.690	$\frac{\eta_{s+ac}}{\eta_{ac}}$
	1.067	1.064	1.064	1.055	1.050	1.050	1.051	1.054	1.056	$\frac{\eta_{s+ac}}{\eta_{ac}}$
					<i>sl. cld.</i>	<i>sl. cld.</i>	<i>cld.</i>			

Gliadin Sols of Double and Triple Concentration.

In view of the above-mentioned investigations on the influence of equimolar quantities of KCl and KI on an acid gliadin sol, it was evident that the differences in viscosities found in aqueous solution disappeared in 44 per cent. acetone.

It was desirable to investigate whether the concentration of the gliadin would have any influence on this phenomenon, the more so as we had observed by studying a large number of data, that there was always a tendency for the KI sol to have a slightly smaller relative viscosity in 44 per cent. acetone than the KCl sol, especially at higher electrolyte concentration (8 m. mol.). These differences always were, however, practically within the region of the experimental error.

Acid sols were made with double and triple protein concentration, and the influence of changing acetone concentration on the relative viscosity of these sols with 8 m. mol. KCl and KI was investigated. Table XIV. gives the results.

It is evident that with increasing protein concentration the differences, found with KCl and KI in 44 per cent. acetone, are practically proportional to the gliadin concentration. However, it struck us that by using sols of higher H-ion concentration, these differences decreased with increasing acid concentration. For example, a sol with 20 mil. eq. HCl did not show any difference in viscosity. It was possible that these differences in viscosity in such an acid 44 per cent. acetone sol did not occur, because there is no lyotropic effect between KCl and KI sols of such high H-ion concentration. To test this possibility it was necessary to study the effect of KCl and KI in aqueous sols of this H-ion concentration. As it was impossible to make these sols containing 8 mil. mol. KCl or KI (because the separated phase settled down), we decided to make sols containing the same quantity of electrolyte and acid, but with the addition of varying quantities of acetone. These sols would be partly stabilised by the presence of acetone, but nevertheless in the smaller acetone concentrations lyotropic effects ought to be found if this effect did exist at all.

TABLE XIV.—INFLUENCE OF 8 MIL. MOL. KCl AND KI ON ACID GLIADIN SOLS OF DOUBLE AND TRIPLE CONCENTRATION IN VARYING ACETONE CONCENTRATIONS.

		0.	6.	10.	12.	15.	18.	c.c. Acetone.
Double concentration	KCl	1'084	1'131	1'148	1'149	1'139	1'090	$\frac{\eta_{s+ac}}{\eta_{ac}}$
	KI	1'044	1'119	1'144	1'146	1'139	1'104	$\frac{\eta_{s+ac}}{\eta_{ac}}$
Triple-concentration	KCl	1'127	1'190	1'212	1'212	1'189	1'108	$\frac{\eta_{s+ac}}{\eta_{ac}}$
	KI	1'070	1'176	1'205	1'207	1'191	1'134	$\frac{\eta_{s+ac}}{\eta_{ac}}$

For this purpose 4.0908 gr. gliadin were dissolved in 50 c.c. of an acetone water mixture (2 : 3); 2.5 c.c. of this sol were pipetted into a volumetric flask, the necessary quantities of acetone, acid and electrolyte were added, and the whole was made up to the mark (25 c.c.) with distilled water. The quantities of acid and electrolyte are given in Table XV. In this way it was possible to make sols of 3, 5, 7, 10, 12 and 16 c.c. acetone per 25 c.c. The sol containing 3 c.c. acetone was slightly opalescent with KCl and opalescent with KI. When still less acetone was added flocculation occurred.

With high H-ion concentration a distinct difference between KCl and KI can be observed in low acetone concentration. This difference decreases towards the maximum. In higher acetone concentrations the lyotropic order is reversed. From this must follow that there still exists a certain lyotropic effect in aqueous medium.

The differences for KCl and KI in acetone medium disappeared not only at higher H-ion concentrations, but also when sols of triple concentration were made without any acid. In this case only sols with 10 and 12 c.c. acetone per 25 c.c. could be made. It was impossible to

prepare sols containing 8 mil. mol. KCl and KI in smaller acetone concentrations, so that it is not certain that there is a lyotropic difference between KCl and KI in aqueous medium in such an unchanged sol.*

TABLE XV.—INFLUENCE OF VARYING ACETONE CONCENTRATIONS ON THE RELATIVE VISCOSITY OF GLIADIN SOLS OF TRIPLE PROTEIN CONCENTRATION CONTAINING 8 MIL. MOL. KCl AND KI.

Without Acid.	7.	10.	12.	16.	c.c. Acetone.
KCl {	<i>flocc.</i>	1'860	1'865	<i>flocc.</i>	$\frac{\eta_s + \text{Ac}}{\eta_{s+\text{Ac}}}$
		1'162	1'166		$\frac{\eta_s + \text{Ac}}{\eta_{\text{Ac}}}$
KI {	<i>flocc.</i>	1'856	1'861	<i>flocc.</i>	$\frac{\eta_s + \text{Ac}}{\eta_{s+\text{Ac}}}$
		1'161	1'165		$\frac{\eta_s + \text{Ac}}{\eta_{\text{Ac}}}$

HCl Conc. 2'18 m. eq.	0.	6.	10.	12.	15.	18.	c.c. Acetone.
KCl {	—	1'717	1'939	1'939	1'758	1'352	$\frac{\eta_s + \text{Ac}}{\eta_{s+\text{Ac}}}$
	1'127	1'190	1'212	1'212	1'189	1'108 <i>cl.</i>	$\frac{\eta_s + \text{Ac}}{\eta_{\text{Ac}}}$
KI {	—	1'697	1'928	1'931	1'761	1'385	$\frac{\eta_s + \text{Ac}}{\eta_{s+\text{Ac}}}$
	1'070	1'176	1'215	1'207	1'191	1'134 <i>cl.</i>	$\frac{\eta_s + \text{Ac}}{\eta_{\text{Ac}}}$

HCl Conc. 20 m. eq.	0.	3.	5.	7.	10.	12.	16.	19.	c.c. Acetone.
KCl {	<i>flocc.</i>	1'410	1'607	1'764	1'908	1'912	1'639	<i>flocc.</i>	$\frac{\eta_s + \text{Ac}}{\eta_{s+\text{Ac}}}$
		1'143 <i>l. op.</i>	1'164	1'182	1'193	1'195	1'166		$\frac{\eta_s + \text{Ac}}{\eta_{\text{Ac}}}$
KI {	<i>flocc.</i>	1'390	1'592	1'754	1'904	1'910	1'648	<i>flocc.</i>	$\frac{\eta_s + \text{Ac}}{\eta_{s+\text{Ac}}}$
		1'127	1'153	1'176	1'190	1'194	1'172		$\frac{\eta_s + \text{Ac}}{\eta_{\text{Ac}}}$

As a lyotropic difference was found at some points of the p_H region, whereas this difference disappeared completely at other p_H , we decided to investigate this influence of the p_H more fully. At the same time, the

* From later determinations we have concluded that in any case in small electrolyte concentrations no lyotropic effects exist in practically iso-electric sols. This was to be expected, because the order of the lyotropic series is reversed at the transition from a positive to a negative sol.

TABLE XVI.—INFLUENCE OF CHANGING H-ION CONCENTRATION ON A 44 PER CENT. ACETONE GLIADIN SOL OF TRIPLE CONCENTRATION WITH VARYING QUANTITIES OF KI AND KCl.

M. Eq. HCl.		0.	2.	4.	8.	12.	16.	M. Eq. Electr.
0	KCl	{ 1'867 1'167	{ — —	{ 1'865 1'166	{ 1'865 1'166	{ 1'866 1'167	{ — —	$\frac{\eta_s + \text{Ac}}{\eta_{\text{Ac}}}$
	KI	{ — —	{ — —	{ 1'863 1'164	{ 1'864 1'165	{ 1'866 1'168	{ — —	$\frac{\eta_s + \text{Ac}}{\eta_{\text{Ac}}}$
0.8	KCl	{ 2'001 1'251	{ — —	{ 1'908 1'193	{ 1'893 1'183	{ 1'885 1'178	{ 1'881 1'176	$\frac{\eta_s + \text{Ac}}{\eta_{\text{Ac}}}$
	KI	{ — —	{ — —	{ 1'908 1'192	{ 1'893 1'183	{ 1'882 1'177	{ 1'881 1'176	$\frac{\eta_s + \text{Ac}}{\eta_{\text{Ac}}}$
1.6		{ 2'108 1'318	{ — —	{ — —	{ — —	{ — —	{ — —	$\frac{\eta_s + \text{Ac}}{\eta_{\text{Ac}}}$
2		{ 2'142 1'339	{ — —	{ — —	{ — —	{ — —	{ — —	$\frac{\eta_s + \text{Ac}}{\eta_{\text{Ac}}}$
2.2	KCl	{ 2'151 1'344	{ 2'031 1'270	{ 1'989 1'243	{ 1'948 1'218	{ 1'930 1'206	{ 1'921 1'202	$\frac{\eta_s + \text{Ac}}{\eta_{\text{Ac}}}$
	KI	{ — —	{ 2'031 1'270	{ 1'984 1'240	{ 1'942 1'214	{ 1'924 1'203	{ 1'913 1'197	$\frac{\eta_s + \text{Ac}}{\eta_{\text{Ac}}}$
3.2	KCl	{ 2'127 1'330	{ — —	{ 1'994 1'246	{ 1'960 1'225	{ 1'940 1'213	{ 1'928 1'206	$\frac{\eta_s + \text{Ac}}{\eta_{\text{Ac}}}$
	KI	{ — —	{ — —	{ 1'990 1'244	{ 1'952 1'221	{ 1'931 1'208	{ 1'919 1'201	$\frac{\eta_s + \text{Ac}}{\eta_{\text{Ac}}}$

TABLE XVI. (continued).

M. Eq. HCl.		0.	2.	4.	8.	12.	16.	M. Eq. Electr.
4	KCl	2'081	—	1'986	1'953	1'935	1'924	$\frac{\eta_s + \text{Ac}}{\eta_{\text{Ac}}}$
		1'301	—	1'241	1'221	1'210	1'201	$\frac{\eta_s + \text{Ac}}{\eta_{\text{Ac}}}$
	KI	—	—	1'983	1'947	1'929	1'918	$\frac{\eta_s + \text{Ac}}{\eta_{\text{Ac}}}$
		—	—	1'239	1'217	1'207	1'200	$\frac{\eta_s + \text{Ac}}{\eta_{\text{Ac}}}$
10	KCl	1'968	—	1'943	1'932	1'924	1'913	$\frac{\eta_s + \text{Ac}}{\eta_{\text{Ac}}}$
		1'230	—	1'215	1'208	1'203	1'197	$\frac{\eta_s + \text{Ac}}{\eta_{\text{Ac}}}$
	KI	—	—	1'948	1'932	1'923	1'914	$\frac{\eta_s + \text{Ac}}{\eta_{\text{Ac}}}$
		—	—	1'217	1'208	1'203	1'198	$\frac{\eta_s + \text{Ac}}{\eta_{\text{Ac}}}$
12		1'956	—	—	—	—	—	$\frac{\eta_s + \text{Ac}}{\eta_{\text{Ac}}}$
		1'223	—	—	—	—	—	$\frac{\eta_s + \text{Ac}}{\eta_{\text{Ac}}}$
20	KCl	1'921	—	1'918	1'914	1'910	1'911	$\frac{\eta_s + \text{Ac}}{\eta_{\text{Ac}}}$
		1'201	—	1'199	1'196	1'194	1'195	$\frac{\eta_s + \text{Ac}}{\eta_{\text{Ac}}}$
	KI	—	—	1'916	1'912	1'907	—	$\frac{\eta_s + \text{Ac}}{\eta_{\text{Ac}}}$
		—	—	1'198	1'195	1'193	—	$\frac{\eta_s + \text{Ac}}{\eta_{\text{Ac}}}$

influence of the quantity of electrolyte added was determined. In the interests of brevity, only the data for sols of triple concentration are given, but analogous determinations were made with sols of double concentration (Table XVI, Fig. 10). From this table it is evident that the difference between KCl and KI sols of equimolar concentration changes with varying H-ion concentration. In a sol without acid, as well as in a sol with high H-ion concentration, the difference disappears. The maximum divergence of the KCl and KI curves is found at about the maximum of viscosity of the sols with electrolyte.

The maximum in the relative viscosity curves shifts to higher H-ion concentrations with the quantity of electrolyte added, as was found before with the dilute gliadin solutions. For one and the same H-ion concentration the difference in relative viscosity between the KCl and KI sols increases with the electrolyte concentration and seems to reach a constant final value.

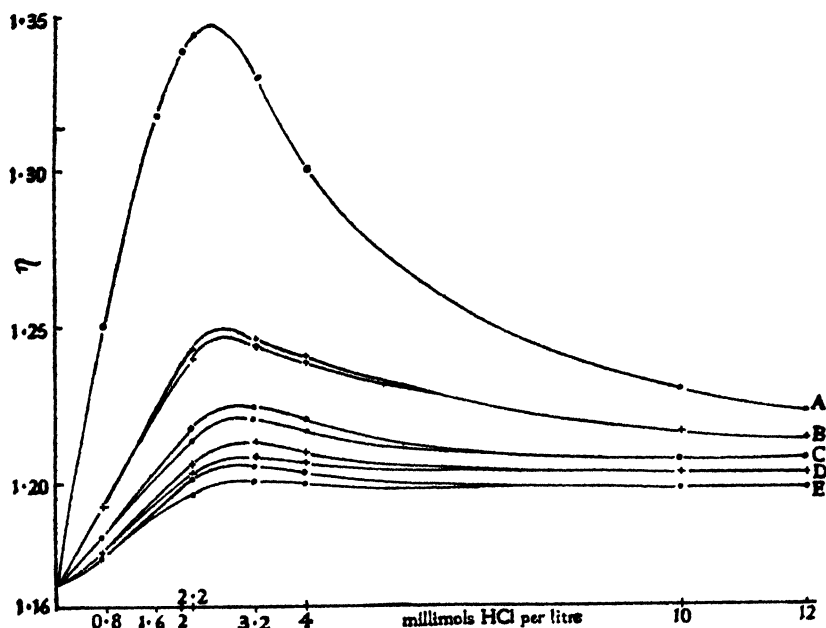


FIG. 10.—See Table XVI.

Curve A = 0 millimol.

" B = 4 "

" C = 8 "

" D = 12 "

" E = 16 "

Determination of the Composition of the Solvation Layer of Uncharged Gliadin in Varying Alcohol Concentrations.

For these determinations we did not use the same gliadin as for our other experiments, but a preparation made from fresh gluten; 3 or 6 gr. gliadin were dissolved in flasks at 60° C. in varying quantities of alcohol of 65 per cent. by volume. After cooling down to 25° C. in a thermostat, the solutions were diluted either with water or alcohol of a temperature slightly lower than 25° C., so that the final temperature after mixing was 25° C. The flasks were stoppered with corks and silverfoil, and held for two weeks in the thermostat. From preliminary experiments it was evident that in this time equilibrium was reached. After this period the original liquid had separated into two distinct layers. The nature of the protein-rich layer was in a high degree dependent on the alcohol percentage of the original solution. Starting from very dilute alcohol, the sediments became more and more liquid with increasing alcohol concentrations in solution. For instance, in the lowest alcohol concentration used in our experiments, the layer was a thick liquid, whereas in alcohol of about 27 per cent. it was very mobile. In alcohol concentrations greater than 60 per cent. the layer was, with increasing alcohol concentration in solution, successively liquid, a perfect gel, tough and finally in alcohol of about 90 per cent. granulated.

After a fortnight the supernatant liquid was completely decanted if possible, and the weight of the remaining sediment was determined. If

complete decantation was impossible on account of the nature of the layer, part of the sediment was transferred into and weighed in another flask.

The protein and the alcohol were then determined in the supernatant liquid as well as in the sediment. For the determination of alcohol, 10 c.c. of the supernatant liquid were pipetted and weighed in a flask and at the same time 10 c.c. were evaporated and dried at 104° C. to constant weight (protein determination). The same method was used for the protein-rich layer, but in this case alcohol and protein were determined in the same sample of known weight. The alcohol concentration of both the layers was determined by the distillation method. Preliminary determinations had proved that this method could very

TABLE XVII. (a).

Total Weight in Grams.	Dry Material 104° C.	Grams Alcohol and Water.	Specific Gravity of Alcohol Dist. 15/15.	Grams Alcohol in Dist.	Alcohol Per Cent. by Weight.	Appearance.	
Analysis of the protein-rich layer.							
6.0606	2.4637	3.5969	0.99818 ×	0.2385	6.70	liquid	I
3.3321	1.2272	2.1049	0.99920 †	0.2120	10.07	"	II
5.8738	2.3493	3.5245	0.99643 ×	0.4798	13.61	"	III
5.4404	2.1104	3.3300	0.99540 ×	0.6240	18.74	"	IV
2.7770	0.7947	1.9823	0.99603 ×	0.5358	27.03	"	V
Weight of 10 c.c. Sol.	Protein Per 10 c.c.	Grams Alcohol and Water.	Specific Gravity of Alcohol Dist. 15/15.	Grams Alcohol in Dist.	Alcohol Per Cent. by Weight.		
Analysis of the supernatant liquid.							
9.8331	0.0379	9.7952	0.99509 ×	0.6674	6.81	—	I
9.7829	0.0533	9.7296	0.99630 †	0.9960	10.24	—	II
9.7154	0.0675	9.6479	0.99058 ×	1.3360	13.85	—	III
9.6612	0.1103	9.5509	0.9789 ×	1.7659	18.49	—	IV
*5.7020	*0.2016	5.5004	0.9740 ×	1.4570	26.49	—	V

† = in 50 c.c.

× = in 25 c.c.

dist. = distillate.

well be used, but much care was necessary on account of foaming. The determinations of the upper layers gave an experimental error of about 0.2 per cent., but even with the protein-rich layer this accuracy could be reached after some practice. Before the distillation of the protein layers some water was added and, after complete evaporation in a bath of saturated CaCl_2 solution, the distillation was repeated twice with newly added water. The protein remainder was then dried at 104° C. and weighed. The alcohol distillate was received in a volumetric flask of 25 or 50 c.c. containing some water, and constantly cooled with running water. Afterwards the flask was made up to mark with distilled water

* In this determination the quantity of sol was only weighed and not pipetted, so the protein content was determined in 5.7020 gr. sol.

at 25° C., and the specific gravity of the distillate was determined in an Ostwald pycnometer.

From these determinations all the necessary data are known for the calculation of the alcohol and water concentration in the protein-rich layer and the supernatant liquid. For this purpose the dry material (protein) was subtracted from the total weight and the percentage of alcohol in the remaining liquid calculated.* Table XVIII. and Fig. 11 give the results.

TABLE XVII (b).

Total Weight in Grams.	Dry Material 104° C.	Grams Alcohol and Water.	Specific Weight of Alcohol Dist. 15/15.	Grams Alcohol in Dist.	Alcohol Per Cent. by Weight.	Appearance of the Layer.	
Analysis of the protein-rich layer.							
5'3461	1'1435	4'2026	0'98203 ×	2'7988	66'60	liquid	A
6'7798	1'6212	5'1586	0'97879 ×	3'4475	66'71	"	B
11'6912	3'5557	8'1355	0'96790 ×	5'5475	68'19	perfect gel	C
6'0670	2'1883	3'8787	0'98975†	2'930	75'54	toughy	D
4'5247	1'6805	2'8442	0'99226†	2'157	75'84	tough	E
8'9929	3'2942	5'6987	0'97312 ×	4'5095	79'13	very tough	F
14'3303	4'6853	9'6450	0'95040 ×	8'1500	84'50	spongy	G
9'5715	1'7410	7'8305	0'95703 ×	7'2707	92'85	granulated	H
Weight of 10 c.c. Sol.	Protein Per 10 c.c. 104° C.	Grams Alcohol and Water.	Specific Weight of Alcohol Dist. 15/15.	Grams Alcohol in Dist.	Alcohol Per Cent. by Weight.		
Analysis of the supernatant liquid.							
8'7470	0'5404	8'2066	0'96747 ×	5'6227	68'46	—	A
8'7847	0'6581	8'1266	0'96775 ×	5'5737	68'58	—	B
8'5652	0'2200	8'3452	0'96463 ×	6'1086	73'17	—	C
8'3052	0'0202	8'2850	0'97903†	6'7882	81'93	—	D
8'2976	0'0175	8'2801	0'97912†	6'7526	81'55	—	E
8'2366	0'0088	8'2298	0'97852†	6'9896	84'93	—	F
8'1544	0'0062	8'1482	0'95789 ×	7'1482	87'73	—	G
8'0055	0'0130	7'9925	0'95572 ×	7'4535	93'25	—	H

† = in 50 c.c.

× = in 25 c.c.

dist. = distillate.

On the horizontal axis of Fig. 11 is plotted the alcohol percentage in the supernatant liquid (dispersion medium), while on the vertical axis the corresponding value for the protein-rich phase (solvation layer) is found.

Curve A represents the equality of the alcohol content of the two layers. At lower concentrations the values of our determinations actually coincide with this curve. Therefore in this case the solvation of the protein particles in the protein-rich layer has the same composition as

* When our experiments were completed, a publication of the Carlsberg Laboratory¹¹ appeared, wherein the same question of composition of layer and supernatant liquid of alcoholic gliadin solutions was studied. These investigators did not get the same results as ourselves. They made their determinations at 0° C. and used another more indirect method for alcohol determinations, as a result of which it is impossible to check their results with ours.

¹¹ G. Haugaard and A. H. Johnson, *Compt. Rend. Laboratoire Carlsberg*, 18, vol. 2, 1930.

the dispersion medium. Any deviation from curve A represents a difference in alcohol composition between layer and dispersion medium. This effect is found in alcohol concentrations of more than 60 per cent.

Curve B represents the values of our determinations in these media. From the first part of curve B, a steady increase in this divergence from curve A by increasing alcohol concentration was to be expected, but the experiments disproved this. At higher alcohol concentrations a decrease in this divergence takes place. This effect, however, must be visualised as an unreality caused by the difficulty of separating the two layers. If part of the supernatant liquid remains in the protein layer, the differ-

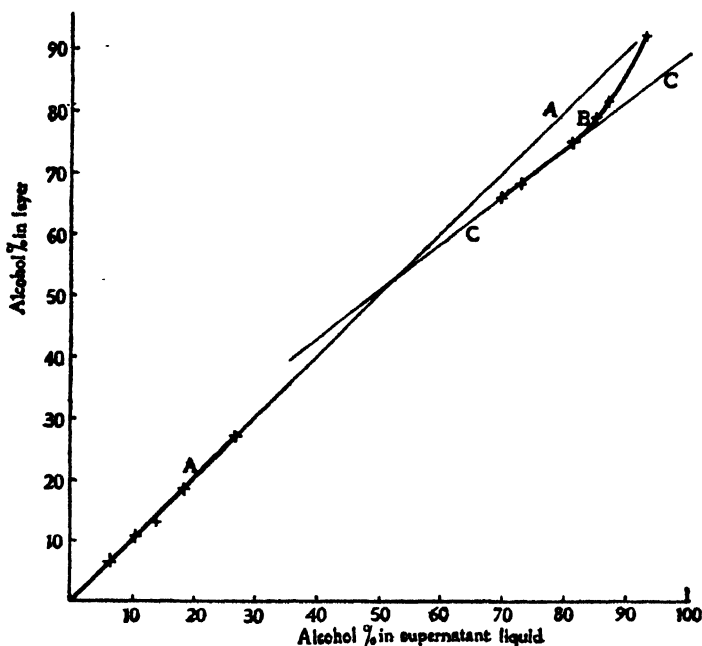


FIG. 11.—See Table VII.

ence in the ratio alcohol-water must naturally diminish. That this is actually the case can be seen theoretically by the increase of the ratio total weight to dry material and, practically, by centrifuging the protein layer in alcohol of about 92 per cent., when this layer separates again into two layers.

Up to 80 per cent. alcohol a proper separation of the two layers was possible, so that the real divergence in composition of the protein-rich layer and supernatant liquid can be expressed by curve C. These curves A and C intersect in an alcohol concentration of about 50 per cent. This is the alcohol concentration at which the maximum in viscosity is found, but we cannot deny that a graphical method, based on only three points, provides too insecure a basis on which to draw any definite conclusions.

Discussion of Results.

The following principal facts can be deduced from the foregoing experimental work on dilute protein solutions.

(a) By increasing the acetone or alcohol concentration in a sol containing equivalent quantities of electrolytes of the same valency, the differences in relative viscosity found in aqueous medium decrease. (Tables III., V., VIII.)

(b) At certain acetone or alcohol concentrations this difference disappears, within experimental error, to reappear in higher concentrations of these media. (Tables III., V., VIII.)

(c) The value of the relative viscosity in the maximum of the acetone (alcohol) relative viscosity curve is dependent on the quantity of electrolytes and on their valency. (Tables IV., VI., IX., X.)

We will now endeavour to give an explanation of these effects. The other experimental facts are for the most part more or less complicated variations of these cases. The phenomena mentioned under (a), (b) and (c) can be considered as the result of a change in solvation through a change in medium. This change in solvation may take place either with the ions or with the colloid particle, or with both.

It is, however, practically certain that the effects are, for the most part, caused by a change in the solvation layer of the particle, and that the effects of the change in solvation of the ions are of minor importance.

The reasons for these may now be discussed. It is well known that for emulsoids the constitution of the solvation layer is of great importance in determining the behaviour of these systems with regard to external influences, whereas on the other hand for ions it is very difficult to indicate circumstances at which the ions alter their solvation. This is the more evident when the magnitude of the solvation layers of ions and emulsoids are compared. For ions, the hydration is but small, and is often not more than one layer of closely bound molecules of water.

This supposition becomes the more probable when we consider the fact that small quantities of electrolytes have no influence, either on the viscosity of water or on the viscosity of water-acetone mixtures. The differences in the viscosities of water-acetone mixtures with and without 10 mil. mol. KI are within the experimental error. Any pronounced influence of acetone-water mixtures on the solvation layer of an electrolyte would certainly appear in the viscosity.

Whereas the foregoing facts only prove that the change in the solvation of the ions in mixed media will be very small, we can show that there is a marked increase in the solvation layer of the colloid particle in these media. When a drop of a separated sol (prepared by adding a quantity of acid too small for total peptisation) is brought under the microscope, and acetone is added, it swells and loses its outlines till at last a water-clear solution is obtained. From these data it is sufficiently clear that the increase or change of the solvation layer of the particle by addition of acetone or alcohol must be the primary cause of the disappearance of the differences mentioned under (a).

As the composition at which the maximum in relative viscosity occurs is always the same for a sol with or without electrolyte, and as at this point it is only the value of the relative viscosity which changes on addition of electrolyte, the explanation of the phenomena obtained with an electrolyte sol can, in the first instance, be referred back to sols without electrolytes.

We will, therefore, first consider this simple case. The increase in relative viscosity of the sol with increasing alcohol concentration must be caused by a gradual increase of the protecting layer.

From our determinations of the composition of the solvation layer and the dispersion medium it is evident that, at least at small alcohol concentrations (up to 27 per cent.), the alcohol concentration of both layer and medium are the same, although we had expected a preferential adsorption of alcohol in the form of alcohol hydrate. The solvation layer of the particle, which in water consists purely of water molecules, will gradually, by increasing the alcohol percentage in the medium, change into a layer of alcohol hydrate molecules.

The increase of the solvation layer by this effect will result in an increase in relative viscosity of the sol. This increase in volume of the layer will reach a maximum at which the maximal concentration of hydrate in the layer as well as in the medium is reached.

In higher alcohol concentrations a completely different effect occurs; there is a preferential adsorption of water, so that the layer is poorer in alcohol than the external phase. As the gliadin is alcoholophobic, the particle will be practically dehydrated in higher alcohol concentrations. If water is added to such a system, it will be preferentially adsorbed by the particle. Approaching the maximum (by diluting the alcohol) the quantity of hydrate will increase, until at last the solvation layer and the external phase have the same composition.

We can therefore say that the left hand part of the viscosity graph represents a system of increasing solvation with increasing alcohol or acetone concentration, whereas the right hand part gives a decrease in solvation with increasing alcohol or acetone in the medium.

Before discussing the influence of electrolyte on an alcohol or acetone sol, it is necessary to consider for a moment the condition of a sol particle in aqueous medium. In an acid gliadin sol the particles are charged positively by the adsorption of H ions on the surface. The following question now arises: Is the surface of the particles entirely or only partly covered by these ions? Supposing the particles to be spherical and the specific gravity of the gliadin to be unity, a rough calculation can give an insight into this question. Assuming that the radius of an H ion is the same as that of an H atom, which is known, it is possible to calculate the area that can be covered by all the H ions of the acid solution. On the other hand, a simple calculation will give the diameter of the globules in which a known quantity of gliadin must be divided, so that the total surface of these globules will be the same as the area that can be covered by all the H ions. In the case of the gliadin solution used in our experiments (1.5 gr. gliadin + 4 c.c. 0.1N HCl) the diameter of the particles must be about 4μ , if the whole surface were to be covered. Now the particles in such a sol are amicroscopical, that is to say, they have a diameter of less than 0.2μ . (Although the particles of an emulsoid sol are invisible on account of their solvation, we can deduce their size from the fact that in a partially discharged sol the drops of the separated phase, which must consist of several particles desolvated to a considerable extent, are on the verge of visibility.) For the same quantity of protein the total surface of the particles with this diameter will be larger than that of particles with a diameter of 4μ . Consequently, it is impossible for the H ions of the acid to cover this surface completely. Moreover, only a small proportion of the H ions in the medium is adsorbed by the protein, as appears from the slight differences in H-ion concentration of the acid solutions with and without gliadin. We may conclude that only a very small proportion of the surface of the particles is taken up by the H ions; these adsorbed H ions are centres of hydration.

Between these centres are large areas unprotected by this hydration caused by charge; we must, nevertheless, assume that these uncharged parts of the surface are nevertheless protected by a hydration layer. This water is attracted as a result of the polar character of the protein molecules.

By addition of equivalent quantities of electrolytes of the same valency to a gliadin sol in aqueous medium, solutions of different viscosity are obtained, *i.e.*, sols of different hydration. In the first instance, we may assume that the discharging effect of equivalent concentrations of ions of the same valency is the same. The differences in viscosity found for these concentrations may indicate that the electrolytes are differently adsorbed by the gliadin particles. This difference in adsorption has been pointed out more than once in the literature of colloid chemistry. The quantity of water expelled from the protecting layer by these different adsorptions cannot be the same; therefore these effects must cause a difference in viscosity of these sols.

It stands to reason that this type of adsorption must be of a different nature from that causing the discharging of the particles, otherwise the state of charge of the particles in solutions containing equivalent quantities of electrolytes of the same valency could not be the same.

We must therefore distinguish between two kinds of adsorptions; the one causing the discharge of the particles through the adsorption of ions of opposite charge, the other being an adsorption of both positive and negative ions or molecules, which causes a change in hydration of the sol without influencing the boundary potential. An indication of the existence of this second kind of adsorption can be found in the investigations of Weiser and Schilow,¹² who have proved that there is no equivalence between the quantities of electrolytes adsorbed by the sol particles. Weiser, and Dhar¹³ also, have shown that a discharged flocculated sol still adsorbs electrolyte. They suggest that this adsorption will only take place after the particles are completely discharged.

In his discussion of the results of cataphoretic measurements Huyzing¹⁴ proves that it is impossible for these two adsorptions to occur the one after another, but that, on the contrary, they will occur simultaneously. We can agree with this point of view if we take into consideration that a large part of the surface is not protected by charge.

Is it possible to give more facts indicating the existence of an adsorption other than that which causes the discharge of the particles? We believe that the clarification by heating of a separated sol may be an indication of this supposition. For the time being we visualise this action as an expulsion of the adsorbed electrolyte by the increased molecular movement.

At the same time, however, we see an indication of this kind of adsorption in the analogous shape of the curves, indicating the addition of alcohol or acetone to gliadin solutions containing surface-active material or electrolytes.

We will now discuss shortly the influence of alcohol and acetone on gliadin sols containing electrolytes. By the addition of alcohol to such a sol there will first occur the same phenomena as that already found

¹² Weiser, *J. Physical Chem.*, **29**, 955, 1925; Schilow, *Z. physik. Chem.*, **94**, 25, 1920.

¹³ Dhar, *Koll. Z.*, **28**, 457, 1924; **35**, 144, 1924.

¹⁴ J. J. Huizing, *Invloed van Electrolyten op de kataphoretische snelheid*, Diss., Utrecht, 1928.

with a sol without electrolyte, *i.e.*, an adsorption of alcohol-hydrate molecules instead of water molecules. By this increase in solvation the gliadin drops (which in water separated out of solution by the dehydrating action of the electrolytes) are once more dispersed. In our opinion, however, this fact cannot give a complete explanation of the phenomena observed with gliadin sols separated by electrolytes in varying alcohol or acetone media.*

We imagine that, coupled with the formation of alcohol hydrate molecules on the surface of the particles, the molecularly adsorbed electrolyte will decrease and at the maximum the electrolyte will be completely thrown off the surface, or will be present in the same quantity.

Since in aqueous solutions of equimolar concentrations, the quantity of KI adsorbed on the surface of the protein is larger than the quantity of KCl, a larger quantity of KI than of KCl will be thrown off the surface by the addition of alcohol. Therefore, the rise in relative viscosity will be larger for the KI sol than for the KCl sol, and in consequence the relative viscosity curve will be steeper for a KI sol. In the behaviour of a sol containing electrolyte in varying alcohol media we see an analogy with that of a sol containing surface-active material in varying alcohol media. In the last-mentioned case it is supposed that the increase of the relative viscosity of a sol containing, for instance, small quantities of resorcinol is caused by the disappearance of the adsorbed substance from the surface of the particle. So far we have not been able to test our supposition that, in the case of sols containing electrolyte, the electrolyte will be expelled from the particle by the addition of alcohol. Ultra-filtration of these alcoholic sols was impossible.

On the other hand, all experiments indicate that a certain sensitivity of the sol for electrolyte still exists at that alcohol or acetone concentration at which the maximum in the viscosity occurs. The effects are, however, the same for equivalent concentrations of electrolytes of the same valency, but different for electrolytes of different valency. The higher the valency of the negative ion the more pronounced will be the influence of the electrolyte.

According to the above explanation, the protecting layer at the maximum is of such a formation that the effects of the molecularly adsorbed electrolytes have disappeared, so there still exists in the medium an essentially different kind of adsorption. Having regard to the differences in relative viscosity found for sols containing equivalent concentrations of electrolytes with anions of different valency, this adsorption must be an ionic adsorption, which only influences the boundary potential. It is readily understood that in these solutions there is still an electric effect, if we consider the fact that, even at a distance, it is possible for an ion to influence the electric field of a centre of charge, which directs polar molecules. Thus in Tables III. and XI. the decrease in relative viscosity at the maximum is only caused by discharging effects. This, therefore, represents the purely electroviscous effect, which in aqueous medium is always coupled with lyotropic influences. Looking at the right-hand part of the relative viscosity-alcohol (acetone) graph we see, firstly, that the same phenomena will occur as with a sol without electrolyte, *i.e.*, a decrease of the hydrate in the solvation layer and a corresponding increase of water in the layer. But coupled therewith there will be a decrease in solubility of the electrolyte (larger

* Especially the fact that gliadin solutions of 44 per cent. acetone are perfectly water-clear, even in the presence of higher electrolyte concentration.

for KCl than for KI), with increasing alcohol concentration. Data are to be found in the literature. Since the solvation layer is relatively richer in water than the dispersion medium, the KCl will be driven to the water-rich phase and adsorbed on the surface of the particles. KI will do the same, but to a less extent. In these media we shall thus get a reversal of the lyotropic series (Table IX.). An analogous explanation can be given for the other monovalent ions. When the lyotropic influence of different electrolytes of the same valency is compared, the strongest adsorbed electrolyte shows the most marked lyotropic influence. The composition of the medium alone decides which electrolyte will be most strongly adsorbed.

If now we consider the effects found in more highly concentrated gliadin sols, we observe, at the maximum, slight differences in relative viscosity between these sols containing equivalent quantities of KI and KCl. These differences are practically proportional to the protein concentration, and could be explained by assuming that there still exist slight lyotropic influences of different electrolytes of the same valency, *i.e.*, the molecularly adsorbed electrolytes will not be thrown off the particle to the same extent. Consequently, the lyotropic effects in diluted protein solutions cannot be zero at the maximum, but must still have a definite value slightly different for every electrolyte. It is also possible to explain these differences in a wholly different manner, still assuming, however, that the lyotropic influences at the maximum are zero or the same for different electrolytes of the same valency. The principal facts found in 44 per cent. acetone sols with higher protein concentrations are:—

(1) The difference in relative viscosity of sols with equimolar quantities of KCl and KI increases practically proportionally to the protein concentration (Table XV.)

(2) At any one protein concentration, but with increasing electrolyte, this difference increases until the sol is practically discharged, to remain practically constant with higher electrolyte concentration (Table XVII.).

(3) The difference between the KCl and the KI curve is maximal when the sols have their maximum viscosities (Table XVII.).

(4) This difference becomes a minimum at the iso-electric point as well as in sols with higher H-ion concentrations (Table XVI.).

The most striking facts are those mentioned under (3) and (4). From these facts it can be deduced that this difference in viscosity is dependent upon the charge of the sol particle. The higher the charge of the sol, the larger will be the difference found by the discharging of the sol with KCl and KI. In an iso-electric sol, as well as in one with high H ion concentration (in which the particles are nearly discharged by the action of the acid) the differences for KCl and KI have disappeared.

To explain these facts it is necessary to consider the phenomena of charging and discharging of a sol in aqueous medium from a general point of view. When acid is added to gliadin the protein is peptised by the preferential adsorption of the H ions and the particles will be charged positively. At the same time the ions of opposite charge (in this case the Cl ions) will be adsorbed by the H ions on the surface of the particle, but to a less extent. These will form a double layer with the H ions, and in this way the charging effect of the H ions will be partly neutralised. By increasing the acid concentration the number of positive centres of charge (*i.e.*, the adsorbed H ions) will increase, but at the same time the discharging effects of the Cl ions will increase also and to a larger

extent. The adsorption of the H ions will reach its maximum at a lower H-ion concentration in the sol than that of the Cl ions. Both the maximum and the drop in viscosity curve after the maximum can be explained by these contradictory forces of the ions.

Consideration must, however, be given to the fact that in aqueous media the electrolytes exercise their lyotropic influence in addition to the effects of their charge. In the case under discussion, therefore, the acid will exercise a lyotropic effect on the gliadin in the same way as KCl and other electrolytes in addition to the effect of its charge. If, however, we assume for a moment that the acid does not show a lyotropic influence, it is to be expected that in higher acid concentrations a final state will be reached, at which the viscosity curve has a horizontal direction, *i.e.*, the viscosity will be independent of further addition of acid. In this region every adsorbed H ion will be opposed by a firmly-bound negative ion. It is, moreover, to be expected that such a sol will not be influenced by the addition of electrolyte; at any rate, if this electrolyte has the same negative ion as the acid used for peptisation and the lyotropic effects of these salts are zero. This is actually the case for sols with such a maximum concentration of alcohol or acetone that the lyotropic effects have disappeared (and in certain other cases not mentioned here). Table XIV.

It is now easy to understand why the viscosities of an iso-electric sol and of a sol discharged either with an excess of acid or with electrolytes in 44 per cent. acetone never reach the same level (Table XIV.), and consequently must have different solvations. In our opinion, the situation can be visualised as follows. Every adsorbed H ion, which is a centre of charge, will attract and direct polar substances (*i.e.*, hydrate molecules) in its field of force. When a negative ion, which also is in possession of a solvation layer, approaches this centre, this ion will be strongly attracted by the H ion. The result will be the formation of a new dipole by the two ions. Consequently, both the ions will lose their solvation. The newly-formed dipole, however, will also have a field of force, and will direct hydrate molecules, but to a far less extent. The hydration of such a dipole must be much smaller than the original hydration of the H ion. In the case of a sol discharged by an excess of acid all the centres of charge on the surface of the particle will be changed into HCl dipoles. Every one of these dipoles will direct a certain number of hydrate molecules. On the other hand, the iso-electric state of a particle will be quite different. In this case, practically no adsorbed H ions are to be found on the surface; nor will there be dipoles which can direct hydrate molecules. Therefore it follows that there must exist a difference in hydration between these two uncharged states of the particle, and consequently in the viscosities of the sols. In aqueous medium these facts will be complicated by the lyotropic influence of the acid.

Applying the foregoing reasoning to the discharging by KCl and KI of a 44 per cent. acetone sol with maximum viscosity, we see that with KCl as discharging agent, the negative Cl ions will be firmly bound in the double layer by the H ions and form HCl dipoles, while in the case of KI the same effect will occur, but of course HI dipoles will be formed. By increasing the KCl and KI concentrations in the sol, the number of dipoles on the surface of the particles will increase until the particles are practically discharged. The addition of more electrolyte after this point will not have any influence on the number of dipoles. As the water binding capacity of HCl dipoles will be larger than of HI dipoles,

we may expect that the same will be the case for the capacity of binding hydrate molecules. Consequently, we may expect an increase in the divergence of the relative viscosity-electrolyte concentration curves with increasing KCl and KI concentration in the sol. This difference will be practically constant when the sol is discharged by these electrolytes. Experimental measurements are in accordance with the above theory. (See (2) above).

The other effects found in higher protein concentrations can also be explained by the formation of dipoles. For instance, comparing sols of the same H-ion concentration, but with different protein concentration, the number of H ions adsorbed on the total surface will be seen to increase proportionally with the protein concentration. On discharging of these sols with KCl or KI, the number of KCl and KI dipoles must increase in direct proportion with the protein concentration. Since there is a difference in solvation between the KCl and KI dipoles, the difference between the relative viscosity curves of the KCl and KI sol will increase proportionally with the number of dipoles, *i.e.*, proportionally with the protein concentration (see (1) above).

By increasing the acid concentration of a sol with maximal viscosity the number of HCl dipoles on the surface of the particle will increase, as a result of the discharging effect of the Cl ions of the acid. On the addition of KCl and KI to such a sol only part of the adsorbed H ions will be free to form dipoles with the Cl or I ions of the added electrolyte, since some of the H ions on the surface have already bound Cl ions of the acid, *i.e.*, the ratio between the HCl and the HI dipoles is increased. By still further increasing the acid concentration of an electrolyte-free sol practically all the H ions on the surface will firmly bind the negative Cl ions of the acid. The result of adding KCl or KI to such a sol will be that practically no HI dipoles can be formed and consequently the factor that gives the differences in viscosity between KCl and KI sols will have disappeared. We can thus deduce theoretically that, with increasing acid concentration in a sol beyond the maximum, the divergence in the relative viscosity of such a sol discharged by KCl and KI will decrease as a result of an increase in the ratio HCl to HI dipoles, and that, in a sol with high H ion concentration, these viscosity curves will run together. This reasoning is, therefore, in accordance with the experimental facts mentioned under (3) and (4).

It is evident that the differences in relative viscosity of KI and KCl sols of higher protein concentrations can be easily explained by the formations of HCl and HI dipoles.

We pointed out above that in 44 per cent. acetone the lyotropic effects of electrolytes have disappeared, and we deduced that the effects of electrolytes in that medium were only caused by a change in the boundary potential. We may now ascertain whether the effects caused by acid and electrolytes to 44 per cent. acetone sols are in accordance with this supposition.

Considering first the effects obtained by adding varying quantities of KCl, K_2SO_4 or $K_4Fe(CN)_6$ to a 44 per cent. acetone sol without acid (Table XII.). For KCl the relative viscosity curve thus obtained will be practically horizontal, while for K_2SO_4 the first traces will give a slight sloping down of the curve. By increasing the K_2SO_4 concentration a rise will occur. The minimum for the $K_4Fe(CN)_6$ curve will be more pronounced. The explanation of these curves is as follows: The concentrations of KCl used in these experiments are insufficient to change

the state of charge of the sol particles. On the other hand, the first additions of K_2SO_4 will take away the charge of the particles and a decrease in viscosity will be the result. This sol, though made without acid, is not quite iso-electric, but has a small positive charge. By further increasing the K_2SO_4 concentration in the sol the particles will adsorb the bivalent negative SO_4 ion and will be gradually charged negatively, and in consequence a rise in relative viscosity will occur. The same will be the explanation for $K_4Fe(CN)_6$. This explanation is based on the fact that the sol is charged slightly positively. The following facts are in accordance with this:—

(a) A slight decrease in the relative viscosity of this sol occurs by the addition of very dilute sodium hydroxide, in other words by adding sodium hydroxide the sol loses its charge and reaches its iso-electric state. We did not find a distinct iso-electric point, but a trajectory of p_H , where practically no change in viscosity occurs.

(b) By the addition of polyvalent electrolytes to the original sol the minima in viscosity do not occur at the same electrolyte concentration. The higher the valency of the negative ion the smaller will be the electrolyte concentration at the minimum in the relative viscosity curve (for K_2SO_4 1.5 mil. eq.; for $K_4Fe(CN)_6$ 0.25 mil. eq.).

(c) The rise in the relative viscosity beyond the minimum will be the larger the higher the valency of the negative ion.

(d) The phenomena found by adding acid to sols containing 10 mil. eq. K_2SO_4 and $K_4Fe(CN)_6$ (Table XIV.).

The above facts confirm the proposition that the 44 per cent. acetone sol without acid must be slightly positively charged, and that it is possible to reverse the charge of a gliadin particle in 44 per cent. acetone by adding polyvalent electrolytes.

Are the facts observed with a sol containing 10 mil. eq. KCl , K_2SO_4 or $K_4Fe(CN)_6$ and changing p_H in accordance with our point of view that all these effects can be explained by a change of charge of the particles. The differences in viscosity of the KCl , K_2SO_4 and $K_4Fe(CN)_6$ sols without acid must be caused by a difference in charge. The K_2SO_4 and $K_4Fe(CN)_6$ sols will be negative, but to a different degree (the charge of the $K_4Fe(CN)_6$ sol will be the higher), while the KCl sol will be charged positively.

By adding acid to a KCl sol the charge of the particles will be increased by the adsorption of the positive H ions, and a rise in viscosity will be the result. On the contrary, the negatively-charged K_2SO_4 and $K_4Fe(CN)_6$ sols will lose their negative charge by addition of small quantities of acid and become electrically neutral. By further increase of the acid concentration the sol will become positively charged for the same reason as with the KCl sol. The discharging of the negatively charged K_2SO_4 and $K_4Fe(CN)_6$ sols by the positive H ions will be the more rapid for the least charged sol, in this case the K_2SO_4 sol. Therefore in this case the viscosity minimum by addition of acid will be found at a lower acid concentration than for the $K_4Fe(CN)_6$ sol, and at the same time the rise in viscosity after this minimum will be quicker for the K_2SO_4 sol than for the $K_4Fe(CN)_6$ sol, because in the first case the bivalent SO_4 ion alone resists the recharging by the positive ions, in the latter case the tetra-valent $Fe(CN)_6$ ion. In this case, too, therefore, all the facts are in accordance with our suppositions, and we may conclude that all the phenomena discussed in this part are due to change of charge of the particles.

There is still another conclusion that can be drawn from the foregoing facts, namely that it is possible to get a negatively-charged sol by adding polyvalent electrolytes at a p_H at which the original sol without electrolyte is charged positively. Thus the real iso-electric point can only be determined in the absence of electrolytes. Similar phenomenon in aqueous medium was pointed out by Kruyt and Tendeloo,¹⁵ working with gelatin sols containing different polyvalent electrolytes. However, in their viscosities lyotropic effects are included. From the data of Tables XII. and XIII. it is evident that the maximum in the relative viscosities for sols without electrolyte, and practically discharged with electrolyte do not occur at the same H-ion concentration. The explanation of this effect is that the percentage increase of the free discharging ions is larger for a sol without electrolyte than for a sol with electrolyte. Since the maximum is formed through the opposing forces of the positive and the negative ions, and the percentage increase of the negative ions (in this case the Cl ions) is smaller for a sol with electrolyte, the maximum will be reached at a higher HCl concentration than with the sol without electrolyte.

In conclusion, we should like to emphasise that the discussion of results must be taken merely as an attempt to explain the phenomena observed. For this explanation it was necessary to introduce a few suppositions. We hope to test these in due course, especially the adsorption of electrolytes in alcohol- and acetone-water mixtures.

Summary.

The following points were studied :—

1. The influence of varying alcohol or acetone concentration on acid gliadin sols containing equimolar quantities of different monovalent electrolytes. A reverse of the lyotropic series was observed in high alcohol and acetone concentrations.
2. The influence of increasing concentrations of mono-valent electrolytes in the viscosity maximum in the alcohol-(acetone)-water diagram.
3. The influence of polyvalent ions in 44 per cent. acetone.
4. The influence of the protein concentration on the viscosities of sols containing electrolyte.
5. The influence of the acid concentration in the sol on the effects mentioned under 2, 3 and 4.
6. The composition of the solvation layer of alcohol-gliadin sols.
7. An explanation of the foregoing facts is given, based on the principle that there exist two kinds of adsorption ; the one being an ionic-adsorption, influencing the boundary potential, the other a molecular adsorption causing the lyotropic effects.
8. In special alcohol or acetone media the last-mentioned effect is the same or zero for electrolytes of the same valency. The differences between sols containing equivalent quantities of electrolytes of different valency can be referred back to different state of charge of the particles.
9. The p_H at which a sol is in the iso-electric state is dependent upon the electrolyte in solution. The iso-electric point can only be stated in electrolyte-free sols.

¹⁵ H. R. Kruyt and Tendeloo. *Kon. Akad. Wet.*, **34**, 4, 1925.

THE OXIDATION OF FUEL VAPOURS IN AIR.¹

BY E. W. J. MARDLES.

DISCUSSION.

At a Meeting of the Faraday Society held on 12th November, 1931, the President (Dr. R. L. Mond) in the Chair.

Professor E. K. Rideal (Cambridge) said that he had listened with great interest to Dr. Mardles and was impressed by the large amount of experimental work which had been carried out. Dr. Mardles was evidently a strong protagonist of "the peroxide" theory of combustion, and he (Rideal) agreed with that view with the proviso that slow combustion and not branching chain combustion was under discussion. The "peroxide" theory *per se* could not be regarded as adequate for explaining slow combustion processes, and he would like to enquire of Dr. Mardles what stress if any he placed on the possible influence of the walls of the containing vessel, apart from the well-known fact that many chain reactions terminate on the walls of the vessel? He asked this question more particularly because he had been interested in the slow combustion of benzaldehyde in solution and with Dr. Brunner in the slow combustion of hexane in the vapour phase. Both of these processes are chain reactions, in both of them the walls terminate chains. How do the chains start? How are the periods of induction, which can be made very lengthy, brought about? It is not sufficient to attribute periods of induction to a known or unknown "antioxygène" as defined by Moureu and examined by Bäckstrom, because the periods of induction can be altered by the insertion of solid materials. During the period of induction Brunner and he found that reaction was proceeding, although Bone in his examination of the autoxidation of methane concluded the contrary. Was it not possible that chain propagation or the conversion of short into long chains at low temperatures at least was dependent on the attainment of a certain bulk concentration of a peroxide-like substance, and was it not possible that this peroxide-like substance was formed both in the bulk phase at high temperatures but also at the surface at low temperatures. These assumptions do at any rate interpret a great many of the more curious phenomena associated with non-branching chain slow combustion.

Dr. E. W. J. Mardles, in reply, said: With regard to the interesting remarks and question of Professor Rideal concerning the influence exerted by the nature of the surfaces exposed to the reactants on the course of the chemical changes during slow combustion, it was found from the experiments with hydrocarbon vapours heated in air for about twenty seconds that apparently only metal surfaces could appreciably affect the results. When the combustion tube was

¹ *Trans. Far. Soc.*, **27**, 681, 1931.

packed with glass, unglazed porcelain, electrode carbon with and without impregnating salts, vanadium oxide, alumina, silica, oxides of lead, etc., the experimental results were not unlike those in the plain glass tube.

Only with iron, copper, lead, nickel, chromium, platinum, etc., and less so with magnesium, aluminium, bismuth or tin were marked differences observed.

The metals all behaved similarly in reducing the yield of intermediate products such as the aldehydes and acids and in increasing the yields of water and carbon dioxide. There does not appear to be, however, any reason to believe that the metals alter the character of the combustion changes. They seem to hasten or crowd the intermediate reactions together, as many of the intermediates cannot be isolated.

With long periods of heating under isothermal conditions at low temperatures when surface reactions presumably are favoured the behaviour was found to be more complex and some oxides influenced considerably the oxidation of the vapours. It does not appear at all clear why some surfaces inhibit and others accelerate. The problem becomes more complicated still with the presence of liquid surfaces; thus, with some oxidations under these conditions, copper for example, can apparently exert both an inhibiting and an accelerating effect according to slight changes in the condition.

The incidence of ionisation on the combustion results was studied. It was found that the introduction of metal foils and gauzes did not change the degree of ionisation or to cause ionisation. Observations of the luminescence emitted by the gaseous mixtures undergoing oxidation showed that when a piece of metal was introduced into the combustion space, if any change was detected the glow tended to concentrate on the metal surface and luminous pulses would extend from this glow at higher temperatures. Similarly with carbon disulphide-air mixtures, when the glass was cleaned from the brown oxidation product the glow would extend from the glass outwards into the combustion space.

The complexity of the whole problem can only be unravelled by future extensive research on surface reactions.

Induction Period.—The period of induction which is known to occur before self-ignition or explosion takes place, and which has been so ably studied by Professor Rideal with Brunner in the case of hexane vapour in oxygen must clearly be associated with peroxide formation. The induction period is most pronounced with pro-knock fuels such as the normal paraffin hydrocarbons which allow the accumulation of organic peroxides during oxidation, whereas with alcohol, ethylene, etc., and other anti-knock fuels, the so-called induction period and peroxidation are not so prominent.

Although peroxidation undoubtedly occurs primarily with ethylene, the organic peroxides react with another fuel molecule autoxidising it to ethylene oxides. Lenher has shown in his study of the oxidation of ethylene² that the formation of ethylene oxide is a principal reaction; and so peroxides do not accumulate but are removed as soon as formed. The oxygen absorption during the induction period of hydrocarbons appeared to be quite vigorous in the cases examined, and the possibility has been considered that with the progress of oxidation nuclei or

² *J. Amer. Chem. Soc.*, **53**, 3737, 1931.

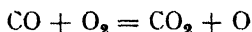
molecular aggregates of organic intermediates have accumulated and afforded further centres of oxidation. Undoubtedly fog formation tends to form from the moment when oxidation begins and appears to sensitise a gas mixture to self-ignition and explosion. From this point of view the duration of the induction period is fixed to some extent at least by the rate of formation and accumulation of nuclei. During the induction period there is a fall not only in pressure but also in temperature, indicating the formation of an endothermic oxidation compound presumably an activated peroxide.

Professor G. I. Finch (*London*) said: Dr. Mardles puts forward the view that when CO is burnt by O₂ an intermediate compound, CO₃, is first formed which then reacts with CO to form 2CO₂. In support of this view he quotes, *inter alia*, Faraday as having found that CO inhibits the oxidation of hydrogen. Faraday did, in fact, discover that CO reduced the rate of flameless heterogeneous combustion of H₂ on a platinum surface, but Langmuir in 1921, and more recently Dr. Bradford, working in this laboratory, have found that the effect is due to CO poisoning the platinum surface. On the other hand, with Dr. Patrick and Dr. Mahler, I have shown that the homogeneous combustion of H₂ by O₂ is actively promoted by CO. Thus Faraday's results cannot be quoted in support of the peroxidation theory, and the fact that CO actually promotes the homogeneous combustion of H₂ seems to me to be destructive of any such hypothesis.

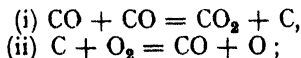
The CO₃ view is open to further objections. The propagation of flame cannot, on kinetic grounds, be explained by any mechanism involving a termolecular reaction. But Born's three-body collision theory, which now rests on a firm and wide experimental basis, forbids the formation of CO₃ as the sole product of a bimolecular reaction. Thus mechanisms such as (a) CO + O₂ = CO₃; CO₃ + CO = 2CO₂, or (b) CO + O = CO₂ are to be rejected, because quantum conditions would otherwise be inconsistent with the law of conservation of energy.

The following schemes involve termolecular reactions and are, therefore, far too slow:—

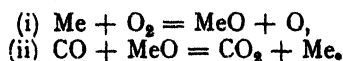
(a) CO + O₂ + 3rd body = CO₃ + 3rd body, etc., or (b) 2CO + O₂ = 2CO₂, or (c) CO + O + 3rd body = CO₂. Bimolecular mechanisms which might be put forward as not conflicting with the three-body collision theory are



or O + electron = O⁻; CO + O⁻ = CO₂ + electron. There is, however, little or no experimental evidence to support either of these views, the former of which is, indeed, in direct conflict with well-established spectroscopic facts. The only reactions, which can reasonably be put forward in explanation of the homogeneous combustion of dry CO — O₂ mixtures in flames and for which direct experimental evidence is available are



both of which have been shown to occur during the homogeneous combustion of dry CO — O₂ mixtures. Patrick and Finch have also found that in the presence of metal vapour the reluctance of dry CO — O₂ mixtures to burn is largely overcome by the formation of metal-oxygen, but not metal — CO complexes, thus:



We have also found experimentally (i) that steam promotes the homogeneous combustion of CO independently of the presence of metal vapour or otherwise, whereas (ii) the rate of combustion of either $\text{H}_2 - \text{CO} - \text{O}_2$ or $\text{H}_2 - \text{O}_2$ mixtures is greatly reduced by metal vapour, (iii) that whilst metal vapour inhibits the formation of some intermediate product other than H_2O_2 formed during the combustion of H_2 to steam, it does not affect the formation of such intermediate product when formed by the decomposition of steam; spectroscopic evidence strongly suggests that this intermediate product is OH. Finally, (iv) preferential combustion of CO occurs in $\text{CO} - \text{H}_2 - \text{O}_2$ mixtures, although in all other respects such mixtures burn homogeneously more rapidly than, but in a manner which is otherwise wholly characteristic of the combustion of, hydrogen but quite different from that of CO. These results show that CO is not burnt by unexcited steam, but reacts partly with excited steam, thus $\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$, and partly with free hydroxyl radicals according to the reaction, $\text{CO} + \text{OH} = \text{CO}_2 + \text{H}$.

Traces of H_2O_2 , proportional in quantity to the amount of combustion which may have occurred are invariably to be found in the combustion products; all the evidence points, however, to such peroxide being purely a bye-product formed as a result of the termolecular reaction $\text{H}_2 + \text{O}_2 + 3\text{rd body} = \text{H}_2\text{O}_2 + 3\text{rd body}$. Professor H. S. Taylor states that, in spite of this direct experimental evidence which so strongly supports the above outlined view of the rôle played by OH, he cannot agree that OH plays any part in the combustion of CO, because Bonhoeffer and Pearson have recently found that the life of the OH radicle is exceedingly short. We will examine Professor Taylor's difficulty in greater detail. I am aware that the results of Bonhoeffer and Pearson's work traverse certain views supported until recently by Professor Taylor. We are, however, concerned at the moment with homogeneous processes occurring in flame. Now I am sure that Professor Taylor, Bonhoeffer, and Pearson fully agree with me (i) that hydroxyl radicals are invariably formed in profusion whenever either H_2 or moist CO burns in flame, (ii) that OH does not cease to exist therein by dissociating into O and H, but (iii) that OH reacts with OH to form, probably, H_2O and O. It follows that the life of an OH radicle must at the very least be equal to the time elapsing between its formation and its first collision with another OH. Hence the life of OH is amply long enough to permit of OH colliding and reacting with CO when $\text{CO} - \text{H}_2 - \text{O}_2$ or moist $\text{CO} - \text{O}_2$ mixtures burn in flames. Therefore, in so far as the issues herein raised are concerned, Professor Taylor's objection falls to the ground.

It would appear that, broadly speaking, Dr. Mardles' main arguments in favour of the peroxidation theory are as follows: (i) colloidal metals decompose hydrogen peroxide, (ii) knocking in an internal combustion engine is inhibited by the presence of metal vapour; therefore, putting (i) and (ii) together, the first stage in the explosive combustion of a hydrocarbon is peroxidation; the metal either prevents the formation of, or rapidly decomposes, the peroxide—surely a somewhat sweeping conclusion. I note that "the peroxidation theory of combustion is not essentially based on the isolation and identification of organic peroxides, but rather on the characteristic behaviour of inhibitors and surfaces and on the phenomena of autoxidation and autocatalysis." Yet it seems to me that the support of organic peroxides is indeed sorely needed

when we find that CO, far from inhibiting, actually promotes the homogeneous combustion of H_2 , and that the combustion of moist CO is wholly unaffected by the presence of metal vapour. Limitations of space do not allow me to extend this discussion to the other examples of combustion studied by Dr. Mardles; it is my intention, however, to do so elsewhere and in greater detail in the near future.

In conclusion, may I be allowed to add that I cannot agree with Dr. Mardles' use of the term "autoxidation" which is, presumably, an abbreviation of "auto-oxidation." CO can oxidise itself to CO_2 , and we are therefore clearly justified in speaking of the auto-oxidation of carbonic oxide. Benzene cannot possibly oxidise itself. To refer to a reaction, in which, for example, phenol is supposed to be formed as a result of the oxidation of benzene by benzeneperoxide, as the "autoxidation" of benzene is misleading and thus surely an example of loose nomenclature which can and does lead to confusion. Also, in the interests of both brevity and clarity, I should like to see "autocatalysis" used more carefully and "moloxide" abandoned.

Dr. Mardles, in reply, said: Professor Finch's remarks are a valuable resumé of his views regarding carbon monoxide combustion.

My particular interest in this substance is its inhibitory action on the slow combustion of several fuel vapours and the fact that whilst behaving as an inhibitor it is autoxidised. I have used the word "autoxidation" in the sense given it by Schonbein, Traube, and other organic chemists, who have laboured to show that when autoxidation occurs with organic compounds it is due to oxidation by an organic peroxide and not by molecular oxygen. As Professor Finch has reminded me I have regarded this phenomenon of autoxidation as the principal foundation of the peroxide hypothesis of slow combustion; and it appears to me that in the slow combustion of most vapours autoxidation plays an important part. Oxidation by "active" oxygen other than molecular oxygen in the case of carbon monoxide cannot be disregarded, and the results obtained throw a favourable light on Bach's view of the formation of CO_3 which acts as a catalyst.

Mr. A. C. G. Egerton (*Oxford*) said: Dr. Mardles has brought together in three papers a number of new facts concerning combustion. His studies provide strong support for the peroxide theory of hydrocarbon combustion, and he is to be congratulated on the wide range of the observations. I am in agreement with his main conclusions, though think that he has sometimes neglected such matters as the influence of surface and of diffusivity of the gases, but he has surveyed a wide field, and each small point could be made the object of a detailed enquiry, and it obviously would have taken years to make a special investigation of each point to find out the more exact meaning of the phenomena from a kinetic standpoint.

The direct combination of the hydrocarbon with the oxygen molecule has always commended itself to me as the most likely step in the initiation of combustion, though it seemed to me a little dangerous to dogmatise too definitely without definite experimental evidence. Recently some experiments Dr. Pidgeon and I have been carrying out at Oxford seem to be supplying direct evidence of the formation of peroxide in the first stage of the hydrocarbon combustion. In the case of ethylene, acetylene, acetaldehyde, etc., recent work by Lenher, Kistiakowsky and Bodenstein, and others, has given evidence of the first process being the direct absorption of the oxygen molecule by the fuel molecule, in the case of

acetylene to form glyoxal, and in the case of acetaldehyde, a peroxide, which being in an active state can propagate a chain reaction. In the case of a saturated hydrocarbon I do not see why the molecule should not become stretched (a predissociation in the photochemical sense) and enabled to absorb an oxygen molecule into its structure when in that state, and so form an active peroxide molecule which subsequently may break up or propagate a chain—this action may possibly have to occur first at the surface. When once reaction has started many paths are open, and hydroxylation as well as peroxidation are possible, as has been shown in the case of ethylene by Hinshelwood and Thompson. In the case of CS_2 , Mr. Thompson has made some interesting kinetic studies, which have a close bearing on the behaviour noted by Dr. Mardles. The self-inhibitory action is certainly of very considerable interest. Dr. Mardles' work raises so many points of interest that it would be unwise for me to pursue them further on account of the late hour.

I would ask whether it is well founded that aldehydes have no action as pro-knockers in an engine, as experiments that I have made have led me to an opposite conclusion, and I thought it was a matter of some importance to be sure as to this action, and intended to make further experiments.

In reply to Dr. Ellis concerning his experiments on the effect of iron carbonyl on carbon monoxide flames, Mr. Egerton said that the gas mixtures were made in a special apparatus, from which they were drawn into the explosion tube, having been mixed with the "anti-knock" by letting in a specific charge from a small volume between two taps; the iron carbonyl being maintained at a specified temperature to provide the vapour pressure required.

Dr. C. A. Naylor (*Buxton*) said: Dr. Mardles has applied the peroxidation theory to hydrocarbon combustion in general, basing his theory on results obtained under widely differing experimental conditions. As the reaction between an inflammable gas and oxygen is influenced so largely by the nature and extent of the walls of the containing vessel it is questionable if the results obtained in the tube experiments can be used to support evidence gained by engine experiments. In addition to the action of the walls of the vessel the physical condition of the fuel molecule must also play a large part in determining the course of the reaction, so that the reaction in an engine cylinder, where liquid drops must persist, may differ completely from the reaction between an inflammable gas and oxygen in a heated tube. This appears to be supported by evidence obtained during a study of hydrocarbon combustion which I have been carrying out for the Safety in Mines Research Board. A very large number of tests on the products of partial oxidation of methane and other hydrocarbon gases have failed to provide evidence of the formation of peroxides, whereas a copious yield of peroxides could be obtained by passing a liquid hydrocarbon, in the form of a spray, through a heated tube. Aldehydes were always detected in the products of oxidation of the gaseous hydrocarbons, and it has been shown by Professor Bone that acetaldehyde accelerates the reaction between ethane and oxygen, whilst we have found that the addition of a small amount of formaldehyde to a methane-air mixture similarly accelerates the reaction. Dr. Mardles has found that aldehydes are anti-knock substances in the petrol engine, which would appear to contradict the evidence obtained by the tube experiments.

The action of inhibitors, when introduced with a gaseous hydrocarbon

into a heated tube, appears to be confined to the surface, and the most efficient inhibitors, as judged by their effect on the rate of reaction, are those which are most difficult to remove from the surface. At high temperatures when the reaction proceeds in the gas phase or when the inhibitor distils from the surface, compounds such as ethyl iodide, ethyl bromide or iodine do not have any marked effect on the reaction between methane and oxygen. Though the peroxidation theory is well supported by certain experiments, further evidence is required before the theory can be applied to such reactions as the oxidation of methane.

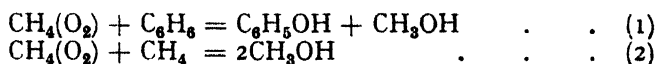
In the determinations of the temperatures of initial combustion given on page 693, Dr. Mardles has used a constant time of heating, and it appears to me that the varying induction or lag periods may have influenced the results. In addition, the formation of fog in the rich mixtures of methane and air, by which the temperature of initial combustion was judged, may have been due to thermal decomposition more than to oxidation.

Dr. Mardles said: In reply to Mr. Egerton and Dr. Naylor regarding the behaviour of aldehydes in the engine it was found from engine experiments in the Ricardo E. 35 variable compression engine 1926, that they exerted very little effect either way on the anti-knock value of a straight-run petrol. It was considered from this that aldehydes could not be held responsible for the knocking action of the normal paraffin hydrocarbons but some more active primary oxidation product.

The combustion of ethane and methane occurs in air at relatively high temperatures, and the introduction of aldehyde vapours which oxidise readily at low temperatures would presumably set up reactions with the methane by autoxidation, but this does not necessarily affirm that aldehydes would induce knocking in an engine. Engine conditions with periods of heating of only a few milliseconds are greatly different from those of the bulb method with times of heating up to an hour, and as Dr. Naylor has pointed out the lag period has less influence. The aldehydes are relatively slow burning and have a smaller temperature coefficient of gaseous reaction.

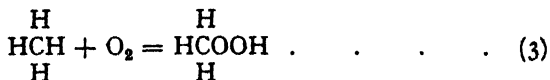
The Peroxidation of Ethane and Methane.—Both ethane and methane oxidise in air only at relatively high temperatures, and although peroxidation cannot be directly demonstrated with ease there is no reason to suppose that there is an entirely different mechanism of combustion for them. On the other hand there is strong evidence based on autoxidation that peroxidation does occur primarily, but on account of the high temperature and high reactivity of the peroxides their life is very transitory.

It will be seen from Fig. II (5) that benzene can exert a marked inhibitory action on the oxidation of hydrogen, and this effect is also found with methane. Similarly excess methane reduces the temperature coefficient of oxidation. These effects can be explained by the following autoxidation equations assuming the formation of a methane moloxide :—



The main oxidation products of methane are methyl alcohol and formaldehyde. It has been shown by Rieche in his investigations on the organic peroxides that methyl hydrogen peroxide yields by decomposition quantities of formaldehyde and methyl alcohol. It is possible

that the moloxide of methane is methyl hydrogen peroxide produced by the simple inclusion of the oxygen molecule between the CH group :—



Another possible source of methyl alcohol is the simple autoxidation of methane by its own peroxide as shown in equation 2 above.

Our experiments with sprays of fuel in air confirm Dr. Naylor's results. Peroxidation and aldehyde formation, etc., were more noticeable than with the vapours, also self-ignition was at lower temperatures, sometimes more than 100° C. below.

Professor Callendar attributed this behaviour to the large surface exposed. Ionisation with sprays was always pronounced. Engine conditions are favourable for spray oxidation even with substances like pentane of low boiling-point. At present engine experiments with hydrogen where presumably nuclei are absent, have not been carried out owing to difficulties of running the engine at full power.

Dr. Oliver C. de C. Ellis (*Sheffield*) said: I have always felt that the hydroxylation theory could not be pressed very much further than the position stated in its first enunciation by Armstrong, where, in closing the "Preferential Combustion" controversy, he said: "We may assume, I think, that the colliding oxygen and hydrocarbon molecules conjugate, if only during a very brief interval of time." The useful thing about this position, which—after the event—no doubt appears axiomatic, is that it may be regarded as the parent not only of the hydroxylation theory but also of the opposing hypothesis that we are called on to consider to-night. It fails to cover the isolation of oxycyanogen compounds from the combustion of cyanogen by Wheeler and Rhead only because cyanogen is not a hydrocarbon. It fails to cover the hydroxylamines in Andrusoff's combustion of ammonia for a similar reason. Let us note, however, that it leads directly not only to the hydroxy methanes of Bone but also with serene impartiality to the peroxide groupings described by Dr. Mardles.

I mistrust the idea of an orderly progressive hydroxylation of methane for the same reasons, or so I suspect, as led Professor H. B. Dixon to reject it. It savours of the ancient Theory of Types. It is incongruous with modern knowledge of the mechanism of combustion. Particularly, I venture to deplore argument based on the constitution of condensates: that is to attempt the history of the dynamic push and thrust of a battle from a post-mortem survey of a static battlefield. Nor can "gas-snatching" during the combustion yield convincing results: burning gas does not considerably halt at a stage of reaction merely because it is locally and partially cooled in the process of removal; there is no real control nor any knowledge of how far the reaction has been checked. These objections, of course, do not apply to adequately planned and equipped examination *in situ* by spectroscopy.

I should like to congratulate Dr. Mardles most warmly, and if I have two suggestions of minor importance to make it is rather to seize the present opportunity than to criticise certain contemporary researches that he has quoted. First, can we clear the ground for a satisfactory definition of *chemiluminescence*? It is fortunate that new investigators are constantly entering upon the subject of combustion, but I think it means that we must guard against a loose use of our special terms. Some

have begun to use this term when they do not wish to say—oh! word of fear!—*Afterburning*. Secondly, can we make absolute the general practice of defining mixtures of carbon monoxide and air or oxygen in terms of their moisture content? It is quite useless, for example, to speak of the speed of flame in a mixture of known composition under the most fully described experimental conditions unless the moisture-content is stated: such a mixture might have any speed less than a characteristic maximum.

Dr. H. J. Emeléus (*London*) said: It should perhaps be pointed out that the experiments in which Dr. Mardles observed autoxidation of such substances as benzene and carbon monoxide were made under conditions where chemiluminescence was occurring. The chemiluminescent oxidation (*e.g.*, of carbon disulphide and hexane) is very much more rapid than the dark reaction, and it is not yet established that the chemical changes taking place under the two sets of conditions are the same. Accordingly, one cannot use autoxidation observed in one case as proof of the formation of peroxides in the dark reaction. A further point of some interest is the fact that in the flame spectra of substances burning in oxygen no spectra characteristic of oxygen atoms or molecules are observed. This is true both of hot flames and of "cold" flames. It suggests that the oxygen molecule ceases to exist as such at the beginning of the oxidation process.

Professor Hugh S. Taylor (*Manchester*) (*communicated*): The intensive investigation of the oxidation of individual hydrocarbons such as acetylene, ethylene and ethane seems to be the next most profitable step to be undertaken in this field. Recent work by Dr. R. Spence in Princeton indicates that some marked success may attend such efforts, while at the same time revealing the complexity of the problem. Spence has found that the kinetics of acetylene oxidation conforms approximately to the Bodenstein mechanism³ for such oxidation processes. One difficulty associated with this conclusion is, however, that the Bodenstein mechanism suggests that the reaction chains are short, whereas the inhibitory influence of packing, narrow reaction vessels and surface coatings on the velocity of reaction suggests long chains. Spence has now shown (forthcoming paper) in what manner a small modification of the Bodenstein mechanism may be made to yield longer chains without major alteration of the reaction kinetics. Extension of such studies to ethylene and ethane is much to be desired.

The studies of oxidation processes under the influence of hydrogen atoms at low temperatures lends support to the peroxide mechanism as the initial step. Hydrogen atoms produce major amounts of hydrogen peroxide from mixtures of hydrogen and oxygen. This may be accounted for on the London-Polanyi-Eyring adiabatic method of treatment of the hydrogen atom-molecule problem.⁴ Energetic room temperature oxidation of ethylene has been induced also by hydrogen atoms and a variety of oxidation products obtained.⁵ The extension of this work to saturated hydrocarbons such as ethane is in progress.

Dr. W. Payman (*Sheffield*) wrote: There is one difficulty in the way of accepting the moloxide theory, and the objection appears to apply also to the hydroxylation theory. According to both of these the primary reaction in the oxidation of a hydrocarbon is between one molecule of the inflammable gas and not more than one molecule of

³ *Z. physik. Chem.*, **12B**, 151, 1931.

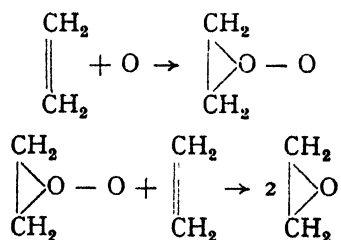
⁴ *Ibid.*, 279, 1931.

⁵ Vernon, *Princeton Thesis*, 1930.

oxygen. But with ethane, one of the gases cited by exponents of each theory, the mixture with air corresponding to the composition $C_2H_6 + O_2$ is not even inflammable at ordinary temperatures and pressures, that is it will not support the independent propagation of flame. I do not know whether this can be explained by the hydroxylation theory, but I understand that Dr. Mardles would explain it by the moloxide theory on the supposition that the moloxide may react with another molecule of fuel and lose a part of its energy and cease to be a catalyst. But the pentane-air mixture $C_5H_{12} + O_2 + 3.8N_2$ is not inflammable at ordinary temperatures and pressures just as the benzene-air mixture $C_6H_6 + O_2 + 3.8N_2$ is not. Further the most rapidly burning mixture of benzene in air contains more fuel than the corresponding mixture of pentane in air.

Dr. S. Lenher wrote: Dr. Mardles' papers on the oxidation of fuel vapours are a valuable contribution to the study of the mechanism of hydrocarbon combustion. The writer's own work on the slow combustion of acetylene⁶ and ethylene⁷ have led him to conclude that the primary process which is common in the slow oxidation of the unsaturated hydrocarbons is that of activation of the hydrocarbon, usually through the formation of an intermediate peroxide compound. However, it may be pointed out that in neither Dr. Mardles' work nor the writer's work on acetylene has any direct experimental evidence been offered to demonstrate the primary formation of a peroxide from acetylene and oxygen. The occurrence of large amounts of carbon monoxide and formaldehyde, the abnormal kinetics of the reaction, and the absence of polymerisation products can all be adequately accounted for by assuming that glyoxal, $C_2H_2O_2$, is the primary product of the reaction. The knocking action of acetylene may be caused by the rapid decomposition of glyoxal, as well as by decomposition of explosive peroxides. Since no direct evidence of peroxide formation in acetylene combustion has been obtained, even at low temperatures, it is desirable to have more information on this point.

Dr. Mardles' suggestion of the formation of ethylene oxide in the combustion of ethylene and oxygen is especially interesting since the writer has recently shown⁷ that ethylene oxide is an important primary product of the oxidation of ethylene. There is no doubt that peroxidation is pronounced in the oxidation of the olefin hydrocarbons; the primary formation of the olefin oxides can only be explained by a reaction of the type,



involving an olefin moloxide. The polymerisation of ethylene⁷ in the oxidation of ethylene is further evidence that peroxidation is the

⁶ Kistiakowsky and Lenher, *J. Amer. Chem. Soc.*, **52**, 3785, 1930. Lenher, *ibid.*, **53**, 2962, 1931.

⁷ Lenher, *J. Amer. Chem. Soc.*, **53**, 2420, 3737, 3752, 1931.

primary process in the oxidation of the olefins. The occurrence of dioxymethyl peroxide as a secondary product in the oxidation of ethylene⁷ shows that peroxidation goes on in the later stages of the oxidation process.

The wide applicability of the peroxide theory of combustion is shown strikingly in Dr. Mardles' papers in which the phenomena of explosive combination are correlated with the more involved processes taking place in slow combustion.

THE ELECTROPHORESIS OF AGAR-GOLD SOLS.

BY E. B. R. PRIDEAUX, M.A., D.Sc., F.I.C., AND F. O. HOWITT, M.Sc., A.I.C. (*University College, Nottingham*).

Received 26th October, 1931.

Agar, a polygalactose containing calcium and the sulphuric group,^{1, 2} is frequently used as a support for dilute aqueous solutions of electrolytes and hence its electrochemical characteristics are of some importance.

The ash of normal agar is reduced from 5 per cent. to 2 per cent. by washing with water but is not further reduced by any such simple treatment as precipitation with alcohol.³ An agar solution contains calcium ions but no sulphate ions. Thus on treatment with potassium oxalate Ca is replaced by K, yielding a derivative capable of gelation.

The physico-chemical characters of agar are in accordance with its constitution of a calcium sulphuric ester of a *d*-galactan. The swelling or imbibition of water by agar gels is repressed by acids and only slightly increased by very dilute solutions of alkali. According to the theories of Proctor, Freundlich and others, swelling is favoured by the formation of ions or ionic micelles which lead to an increased osmotic pressure in the interior. Hence, agar exhibits only slight combination with acids and alkalis.² Agar itself has a steady p_H of about 5.4 to 5.7, but unlike gelatin, agar exhibits only a slight tendency either to accept or donate hydrogen ions in dilute solutions.²

With agar sols of a concentration not exceeding 2 to 7 per cent. the relative increases of viscosity $(\eta - \eta_w)/\eta_w$ and also the densities, are linear functions of the concentration.³ The viscosities of these solutions are, however, much greater than the values calculated by the equation of Einstein or, if electrolytes are present, by that of Smoluchowski.⁴

$$\frac{\eta - \eta_0}{\eta_0} = \frac{5}{2} \phi \left[1 + \frac{1}{\kappa r^2 \eta} \left(\frac{D\xi}{2\pi} \right)^2 \right],$$

in which κ is the conductivity of the solution, r the radius of the particles, ξ the electrokinetic potential of the double layer, and D the dielectric constant of the medium. This equation, strictly speaking, applies only to suspensoids, the solution volume ϕ and radius r of which are known but it can also be used in a semi-quantitative manner for lyophilic colloids.

¹ Haas, *Biochem. J.*, **15**, 469, 1921.

² Fairbrother and Masters, *J. Chem. Soc.*, **123**, 1412, 1923.

³ Krut and de Jong, *Kolloidchem. Beih.*, **28**, Hefte 1 and 2, 1928.

⁴ *Koll. Zetschr.*, **18**, 190, 1916.

The characteristic effect on the ξ -potential will only come into evidence when the conductivity is not too high, *i.e.* at low concentrations of electrolytes. These are found to depress the relative viscosities of agar sols, while non-electrolytes such as urea and sucrose in corresponding concentrations do not affect the relative increase of viscosity due to the agar. Thus, it is evident that electrolytes diminish the ξ -potential by adsorption of the ion having the opposite sign to that of the micelle.

Now it was shown by Kruyt and de Jong³ that the fall in relative viscosity depended only on the kation since it increased with increase of valency of this but did not vary with increased anionic charge. These facts show that the agar is negatively charged. The higher the positive valency, the greater the discharging effect per equivalent, so that the relative viscosities at equivalent salt concentrations are in the order :



The curves of $\frac{\eta - \eta_0}{\eta_0}$ against milliequivalents of added salt fall into four bundles which show a stepwise diminution in the relative viscosity —increases due to agar, namely,

$a > b > c > d$ where

- (a) is K, Na, NH_4 , chlorides and ferrocyanides.
- (b) is Ba, Sr, Mg, Cd chlorides and sulphate
- (c) is La and $Co(NH_3)_6$ salts.
- (d) is $Pt(en)_3(NO_3)_4$ (en = ethylene diamine).

As it follows from the equation of Smoluchowski, that diminution in micellar charge leads to diminished viscosity, these results prove the discharging effect of the kations. The relative diminutions in viscosity brought about by HCl and KOH are between those of KCl and $BaCl_2$. Hydrogen ions therefore have less discharging effect than potassium ions yet it is recorded that H ions are strongly adsorbed. Also OH^- ions diminish the discharging effect due to K^+ and they are also said to be strongly adsorbed. There appears to be a conflict of evidence here, since the evidence of swelling and p_H shows that these ions in cold and fairly dilute solutions are *not* strongly adsorbed. If this is so, their relatively slight effect upon viscosity would be comprehensible.

Electrophoresis.

A direct proof of the negative charge on agar was desirable and was given by Kruyt and de Jong³ in an apparatus modified from that of Burton. In order to avoid convection currents and diffusion of alkali or acid from electrodes, these were set in a 2 per cent. agar sol containing 1 per cent. of $CuSO_4$ and at the bottom of two smaller U-tubes attached to the sides of the electrophoresis U-tube. In this a beam of light travelling axially downwards revealed the agar sol by a luminescence due to the Tyndall effect. A velocity of 7.5 mm. in four hours was recorded but the potential gradient was not stated. A concentration of 1 m. eq. of $Co(NH_3)_6 Cl_3$ per litre reduced this velocity to 6.0 mm. whilst 10 m. eq. reduced it to 2.0 mm.

Agar-gold Sols.

Our experiments were designed to investigate the effects, if any, of changes of $[H^+]$ on the electrophoretic velocity of agar. In order to

render the boundary visible we have added a lower concentration of gold sol since much previous work has shown that colloidal gold as well as other ultramicroscopic and microscopic particles, *e.g.* quartz and glass behave electrophoretically like the lyophilic colloids in which they are suspended. It has also been necessary to add a buffer solution to stabilise low values of $[H^+]$. Sodium acetate was suitable for this purpose.

The agar was prepared from the best commercial product free from gelatin and having 2.2 per cent. of ash, 19.6 per cent. of moisture, therefore 2.75 per cent. of ash on the dried material. After dialysing for forty-eight hours against distilled water it had 1.8 per cent. of ash (2.4 per cent. on the dried material) and 25 per cent. of moisture.

The solutions used for electrophoresis contained 0.1 per cent. of dry agar, 0.02 per cent. of gold sol and were 0.03 *N* in acetate buffer. Acid

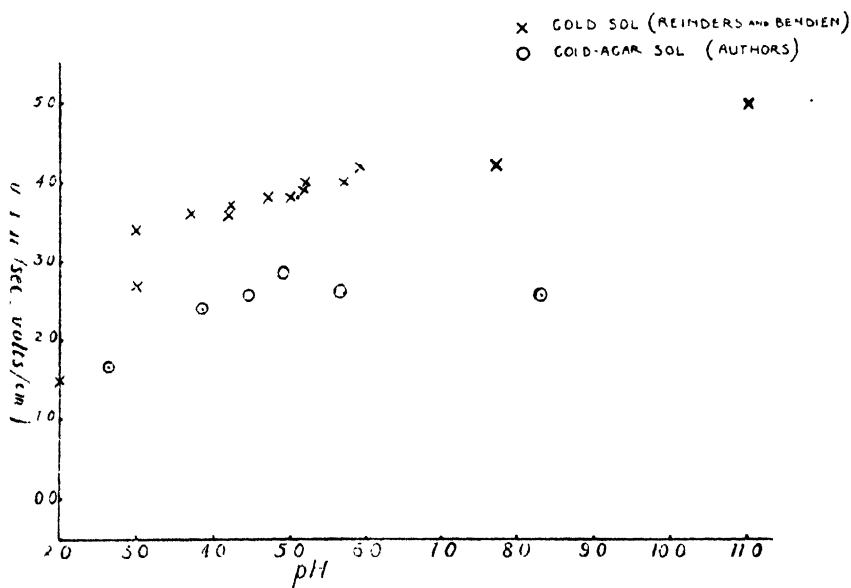


FIG. 1.—Effect of p_H on the Electrophoresis of Gold and Gold-Agar Sols.

or alkali were added and the p_H values determined with the hydrogen electrode.

The *apparatus*, designed for visual observation of the motion of the gold-colloid surface, has been previously described⁵. The potential fall at the applied voltage was 3.75 volts./cm. and this multiplied by 3.6 gives the factor 13.7 by which the experimental velocities were converted into μ /sec., volts./cm. The results were further corrected to 18° by means of the viscosity ratio of water $\frac{\eta_t}{\eta_{18^\circ}}$ since experience has shown that the velocities will only be affected by this temperature coefficient and not by the higher viscosities of the sol as determined in the Ostwald viscometer. The surfaces moved up in the anodic limb and down in the cathodic, showing a negative charge. The results are given in Table I. and are shown in the graph.

⁵ *J. Sci. Instr.*, **7**, 90, 1930.

TABLE I.—VELOCITIES OF AGAR-GOLD SOLS.

p_H	mm./hr.		Mean.	t°	$\mu/\text{sec. Volts/cm.}$ at 18° .
	Up.	Down.			
2.63	10 *	35	22.5	17.5°	— 1.67
3.86	29	35	33.0	18°	— 2.41
4.44	38	32	35.0	18°	— 2.55
4.90	38	40	39.0	18°	— 2.84
5.65	32	39	35.5	18°	— 2.60
8.30	30	36	33.0	16°	— 2.55
					— 2.59 average.

With the doubtful exception of the first experiment in which the "down" velocity was uniform with the others but the "up" velocity was obviously abnormal, the experiments show that the negative charge of agar is not influenced by changes of p_H beyond the limits of experimental error.

The ξ -potential corresponding to the mean velocity may be calculated by the Helmholtz-Lamb equation,

$$\xi = \frac{6\pi\eta v}{EK_D} \quad \text{or} \quad \frac{4\pi\eta v}{EK_D}.$$

In which v/E is the velocity in absolute units under unit potential gradient, K_D is the dielectric constant and η the viscosity, both taken as those of pure water. Introduction of the numerical values and constants leads to $\xi = 0.038$ or 0.057 volts, according as 4π (the constant usually assumed) or 6π are included.

Note.—According to Debye and Hückel 4π refers to a cylindrical and 6π to a spherical micelle.

Gold Sol.

The electrophoretic velocity of gold sol according to Burton is 2.2 $\mu/\text{sec.}$, volts/cm. giving a ξ -potential of 0.032 volts. The results of later workers, however, have proved that the velocity and ξ -potential are higher than this. The velocities will be expressed uniformly in the above units. Thiessen and Heumann⁶ found that $v = 3.0$ in a neutral solution and that it is reduced by electrolytes and increased by Na_2CO_3 . Fuchs and Pauli⁷ found 2.5 to 3.5 at 25° . A comprehensive investigation of the effect of p_H changes is due to Reinders and Bendien.⁸ The 0.01 per cent. gold sols used by these workers were prepared by phosphorus in ether, formaldehyde or arcing and were present in dilute electrolytes: 0.001 N -NaOH, 0.0001 N -HCl or 0.0003 N -KCl. The p_H was varied by additions of small quantities of acids or alkalis. The velocities under a potential fall of 110 volts were observed in a U-tube. The velocities are given in two series, reproduced in Table II., and are plotted in the graph.

⁶ *Z. anorg. chem.*, 148, 382, 1925.

⁷ *Kolloid-Chem. Beih.*, 21, 412, 1926.

⁸ *Rec. Trav. Chim.*, 47, No. 11, 1928.

* Some diffusion.

TABLE II.—ELECTROPHORETIC VELOCITIES OF GOLD IN μ /SEC. VOLTS/CM. AT 25°. REINDERS AND BENDIEN, 1928.

p_H	.	3.0	4.2	5.0	5.2	7.7	11.0			
v	.	-3.4	-3.6	-3.8	-3.9	-4.2	-5.0			
p_H	.	2.0	3.0	3.7	4.2	4.7	5.2	5.7	5.9	11.0
v	.	-1.5	-2.7	-3.6	-3.7	-3.8	-4.0	-4.0	-4.2	-5.0

It will be seen that velocities are only slightly affected by changes of p_H but rise slowly as this is increased.

Another series shows that the velocity is hardly affected by KCl up to 0.01 *N* but is slightly diminished by a concentration of 0.02 *N* of the salt. Very low concentrations of gelatin have a great effect upon the velocity, lowering it in all sols and reversing it when $p_H \leq 4.2$ and $C \geq 0.005$ per cent. Between 0.05 and 0.10 per cent. of gelatin the gold behaves as protein, the characteristic velocity of which is highly dependent on p_H . Casein has a somewhat similar effect; a concentration of 0.02 per cent. at p_H 3.7 changes the velocity of gold⁹ from -3.6 to +1.9. If a similar effect is assumed in the case of agar then our results give the velocity of this colloid. This assumption is supported by the observation that at all p_H values the velocity on the gold alone is uniformly greater than that of the gold-agar. If the gold were not coated with agar, then, in the upward moving boundary, it would outstrip the agar and the characteristic velocity of the gold alone would be observed. The velocity of agar is such as would be expected of a colloidal substance whose negative charge is due to a partial ionisation of calcium the ions of which, however, remain bound near the surface as long as the cyclic structure due to co-ordination is not broken up, *i.e.* as long as the substance retains its characteristic power of gelation. Such a complex should be, as was found, only slightly affected by moderate changes of $[H^+]$ in respect of the physical properties enumerated above.

Summary.

The available evidence as to the chemical and physico-chemical properties of agar leads to the following views.

Agar is a calcium sulphuric ester of a hemi-cellulose, the cyclic structure of which is responsible for the power of gelation. This is lost when the agar is hydrolysed by hot acids. The negative charge is due to partial dissociation of the calcium ions which are co-ordinated to the molecule. The charge so produced on the residue or ionic micelle remains constant over moderate variations in $[H^+]$ or $[OH^-]$ as is shown by the comparatively slight effect of these ions upon the viscosity ratio and more directly by the constancy of the electrophoretic velocity in solutions of variable $[H^+]$. The absence of any appreciable amphoteric character is thus demonstrated and concurrently the suitability of agar as a support in investigating ionic diffusions of dilute acid and alkali.

⁹ See also Freundlich and Abramson, *Z. physikal. Chem.*, **133**, 5, 1928.

GLASS ELECTRODE STUDIES: SOME CUPRIC HYDROXY-ACID COMPLEXES.

BY CHARLES MORTON.

Received 28th October, 1931.

It is commonly supposed that in Fehling's solution the copper is present as a complex anion, and attempts have been made by Masson and Steele,¹ Pickering,² and Packer and Wark,³ to isolate the blue complex by fractional precipitation with alcohol from neutralised solutions of cupric tartrate. Similar analytical methods have been used by Pickering⁴ and Wark⁵ in the investigation of the supposed cupricitrates, cuprimalates, etc. The identity of these salts has recently been denied by Dumanski and Chalisew.⁶ In an attempt to confirm their existence by a physical method, E. E. Wark and I. W. Wark,⁷ overlooking the fact that the normal electrode potential of copper is positive with respect to hydrogen, sought to follow the course of the neutralisation of various cupric hydroxy-acid salts by means of the hydrogen electrode. It is clear from their published curves that the potentials which the authors observed—potentials which, as measured against the saturated calomel electrode, reversed at neutrality—were not those of the hydrogen electrode.

In the present work, the neutralisation curves of a number of cupric hydroxy-acid salts have been determined by means of the glass electrode. The ballistic system of measurement recently described by the author⁸ was employed, a condenser of 0.5 microfarad capacity being used with a constant charging period of thirty seconds. Measurements were also made by means of a Dolezalek electrometer having a maximum sensitivity of about 1000 mm. per volt at 1 metre. A preliminary titration of 100 c.c. of the universal buffer solution of Prideaux and Ward⁹ with 0.2 N. sodium hydroxide solution was carried out, and a calibration curve constructed from which the p_H value corresponding to a given electrometer deflection could be read directly.* The calibration serves to eliminate errors due to non-linearity both of the E.M.F.- p_H relationship of the glass and of the potential-deflection relationship of the electrometer. The method gives results equal in accuracy to those obtained by a null potentiometric method, and is more convenient when an electrometer of long period is used.

The neutralisation curves are shown in Figs. 1 and 2. In each case, to 10 c.c. of 0.1 M. cupric sulphate solution, excess of the sodium salt

¹ Masson and Steele, *J.C.S.*, **75**, 725, 1899.

² Pickering, *ibid.*, **99**, 169, 1911.

³ Packer and Wark, *ibid.*, **119**, 1348, 1921.

⁴ Pickering, *ibid.*, **97**, 1837, 1910; **99**, 1347, 1911; **101**, 174, 1912.

⁵ Wark, *ibid.*, **123**, 1815, 1826, 1923; 1753, 1927.

⁶ Dumanski and Chalisew, *Kolloid Z.*, **47**, 121, 1929.

⁷ E. E. Wark and I. W. Wark, *J.C.S.*, 2474, 1930.

⁸ Morton, *J. Sci. Inst.*, **7**, 187, 1930.

⁹ Prideaux and Ward, *J.C.S.*, **125**, 426, 1924.

* A more convenient universal buffer mixture for this purpose has recently been described by Britton and Robinson, *J.C.S.*, 1456, 1931.

of the hydroxy-acid was added, and the reaction mixture was diluted so that the solution was approximately 0.01 *M.* with respect to copper. The titrations were carried out with 0.1 *N.* sodium hydroxide solution. The molar ratio of hydroxy-acid anion to copper in the reaction mixtures varied from 5 : 1 for the less stable solutions to 1 : 1 for the more stable salts. In the titration of the tartrate, citrate, malate, and salicylate solutions (Fig. 1) two inflections appeared in the course of each neutralisation curve. The first, which was reached when 1.0 (citrate, malate, salicylate) or 1.25 (tartrate) equivalents of alkali had been added, presumably marks the completion of the process of complex formation: the second occurred in all cases when the theoretical amount (2 equivalents) of strong base required for complete alkaline decomposition had been added. On back-titrating the strongly alkaline solutions with 0.1 *N.* hydrochloric acid the inflections reappeared in the reverse order.

The changes in copper-ion concentration during the earlier stages of the neutralisation were followed by means of the copper electrode. The potentials observed showed that the copper-ion concentration diminished at first slowly, but later rapidly as the neutral point was approached.

The inflection point in each case coincided with the first inflection point in the corresponding neutralisation curve. There is, in fact, a close parallelism between changes of cuprion and of hydrion concentration. Whether or not a simple relationship exists was not discovered, for at this stage it was learned that Dr. Britton was engaged in similar work, and the experiments were discontinued. A few dialysis

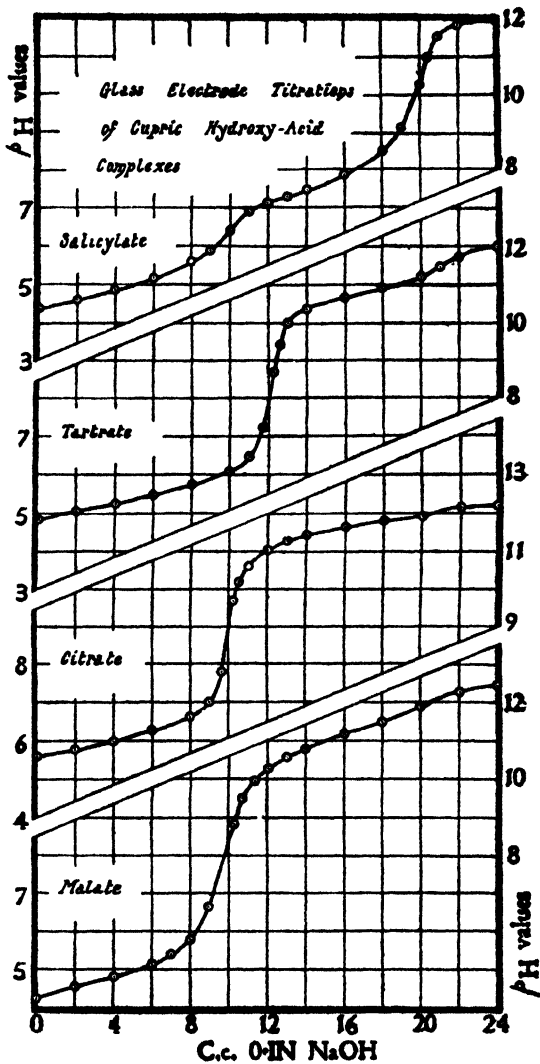


FIG. 1.

experiments were carried out, using Whatmans dialysing shells, and it was found that from the acid solutions the whole of the copper could be removed by dialysis: slightly alkaline solutions, on the other hand, yielded almost colourless diffusates, and the dark blue dialysates flocculated on standing. The transition from electrolytic to colloidal solution or *vice versa*

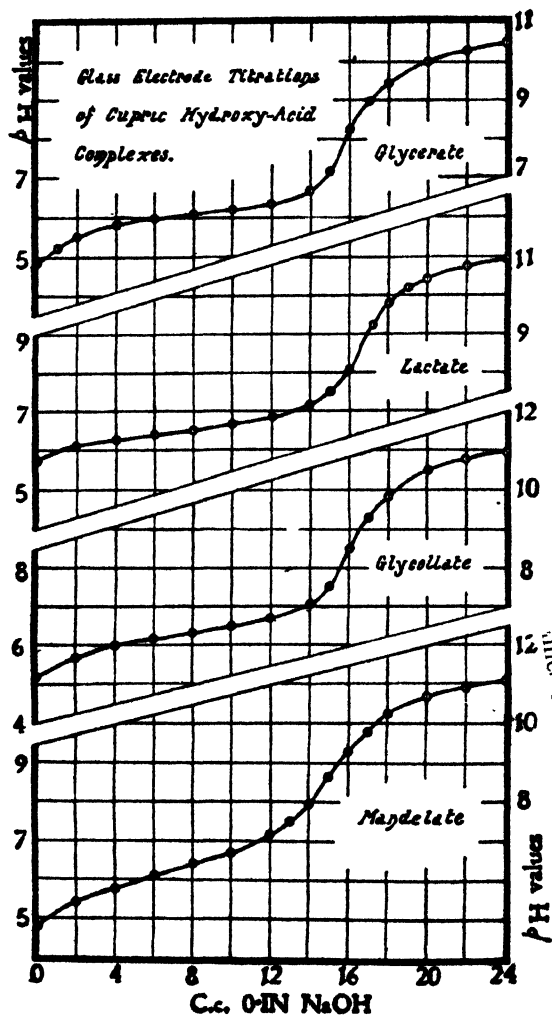


FIG. 2.

whilst moving from the cathode, was unable to penetrate a collodion sac surrounding the anode. In view of the discovery of heterogeneous equilibria in the solutions, the analytical procedure employed in the precipitation of the supposed cupritartrates, etc., must be regarded with suspicion.

In the important paper referred to, Britton, judging by analogy from

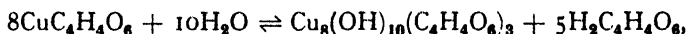
versa is reversible, and takes place whenever the reaction of the solution is changed.

These results may be interpreted in various ways. If the theory of the formation of complex anions be adopted, it must be supposed that the first inflection corresponds with the formation of the neutral cupritartrate, cuprictartrate, etc., and the second with its subsequent decomposition by excess of alkali. The evidence in favour of this view appears to be based solely on the observation of Kahlenberg¹⁰ and Masson and Steele (*loc. cit.*) that, under the influence of a potential gradient, the complexes migrate towards the anode. As Britton¹¹ has pointed out, the cataphoretic behaviour may equally well be due to the colloidal nature of the complex. In agreement with this suggestion, Dumanski and Chalisew found that the blue complex of Fehling's solution,

¹⁰ Kahlenberg, *Z. physik. Chem.*, **17**, 586, 1895.

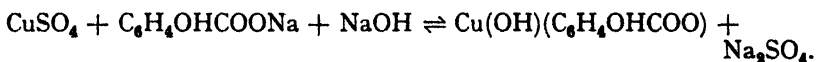
¹¹ Britton, *J.C.S.*, 269, 1926.

the behaviour of the tartrates of a number of weak inorganic bases, suggested that the complex tartrate of Fehling's solution is essentially basic in nature. This view is in accord with our knowledge of the general physical and chemical properties of the cupric hydroxy-acid complexes. The colour and absorption spectra of the "cupritartrates" (which resemble those of basic copper sols), their amorphous nature, their almost unlimited solubility, and the fact that, in certain cases at any rate, a change in composition can be effected by washing, are accounted for if it be supposed that these precipitates are solid sols of basic copper tartrate in excess of alkali-metal tartrate. Again, the fact that excess of sodium salicylate is necessary to prevent the precipitation of cupric hydroxide from neutralised solutions of cupric salicylate is readily explained on the assumption that the process of neutralisation consists in the reversible formation of basic copper salicylates by progressive alkaline hydrolysis, and that in the absence of excess of one of the products of hydrolysis—the hydroxy-acid anion—alkaline decomposition is complete. Similar considerations account for the ready solubility of cupric tartrate—a sparingly water-soluble salt—in sodium tartrate solution. The essential reaction leading to dissolution of the salt is probably the formation of a neutral soluble basic tartrate by hydrolysis,



the function of the sodium tartrate being to remove the liberated acid from the sphere of action in the form of hydrotartrate, and thus to enable the reaction to proceed to completion from left to right. In agreement with this view, it is found that the solution is acid to litmus, and requires for neutralisation 1.25 equivalents of sodium hydroxide per g. atom of copper, regardless of the amount of sodium tartrate present.

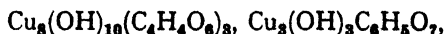
Assuming Britton's view of the nature of the cupric hydroxy-acid complexes to be correct, the initial reaction which takes place in the titration of, *e.g.*, the salicylate solution may be expressed thus:—



The inflection which marks the completion of this reaction does not appear in the "hydrogen electrode" titration curve of Wark and Wark. When the theoretical quantity of alkali required for complete decomposition in the sense of the equation,

$\text{Cu}(\text{OH})(\text{C}_6\text{H}_4\text{OHCOO}) + \text{NaOH} \rightleftharpoons \text{Cu}(\text{OH})_2 + \text{C}_6\text{H}_4\text{OHCOONa}$, had been added, a second and more marked inflection appeared in the neutralisation curve. The non-precipitation by excess of alkali is due to the fact that, as demonstrated by dialysis experiments, the product of decomposition is peptised by the hydroxy-acid anion, and passes into colloidal solution.

From the positions of the inflection points in the neutralisation curves of the tartrate, citrate, and malate solutions it may be inferred that the deep blue complexes have the composition,



and $\text{Cu}_2(\text{OH})_2\text{C}_4\text{H}_4\text{O}_6$ respectively. The fact that, in these curves, the second inflection corresponding with the alkaline decomposition of the

salts is barely discernible, suggests that these compounds are considerably more stable than the salicylate complex—a conclusion which is borne out by a general study of the properties of the solutions. The alkaline solution obtained in the titration of the salicylate was emerald green (a colour which suggests the presence of a mixed cupric and cuprous oxide sol) and, although stable at air temperature, yielded a copious precipitate of cuprous oxide on boiling. Those obtained in the tartrate, citrate, and malate titrations, on the other hand, were deep blue, and were unchanged on boiling in the absence of reducing sugars.

The behaviour of the glycerate, lactate, glycollate, and mandelate solutions (Fig. 2) in the presence of caustic alkalis differs from that described above, and resembles that of the inorganic cupric salts. In each case the neutralisation curve shows only one inflection: this appeared when about three-fourths of the theoretical amount of alkali required for complete decomposition had been added. A blue basic precipitate appeared in each titration: in the case of the glycerate solution, however, this redissolved in the neighbourhood of the inflection point. Precipitation of the glycollate, lactate, and mandelate solutions by alkali could be prevented by the addition of large excess of the sodium salt of the hydroxy acid. Britton¹² found that, in the titration of copper sulphate with caustic alkalis, an inflection occurred, and precipitation was complete, when three-fourths of the stoichiometric amount of alkali had been added: by means of a subsequent phase rule study¹³ it was shown that the precipitate was a definite basic salt, $4\text{CuO} \cdot \text{SO}_3 \cdot 4\text{H}_2\text{O}$. It seems probable that no stable complexes are formed with glyceric, lactic, glycollic, and mandelic acids, and that the inflection corresponds with the formation of the basic sulphate. The fact that, in the presence of large excess of hydroxy-acid salt, the basic salt is not precipitated, may be attributed to the well-known peptising and protective properties of the hydroxy-acid anion.

Summary.

(1) Electrometric measurements by means of the glass and copper electrodes, indicate that in neutralised solutions of cupric tartrate, citrate, malate, and salicylate, the basic complexes $\text{Cu}_2(\text{OH})_{10}(\text{C}_4\text{H}_4\text{O}_6)_3$, $\text{Cu}_2(\text{OH})_8\text{C}_6\text{H}_5\text{O}_7$, $\text{Cu}_2(\text{OH})_8\text{C}_4\text{H}_4\text{O}_6$, and $\text{Cu}(\text{OH})(\text{C}_6\text{H}_4\text{OHCOO})$ are present respectively. In alkaline solution the complexes are decomposed with the formation of highly basic hydrosols.

(2) There is no electrometric evidence of the formation of stable cupric complexes with glyceric, lactic, glycollic, or mandelic acids: the apparent stability of the cupric salts of these hydroxy-acids in the presence of caustic alkalis is due to the peptising properties of the hydroxy-acid anion.

The author desires to express his indebtedness to Dr. J. C. Crocker for the kind interest he has taken in the work. A grant from the Dixon Fund of the University of London is gratefully acknowledged.

Chelsea Polytechnic.

¹² Britton, *J.C.S.*, 2148, 1925.

¹³ Britton, *ibid.*, 2796, 1925.

THE PHOTOCHEMICAL REACTION OF CARBON MONOXIDE WITH AMMONIA AND WITH AMINES.

By H. J. EMELÉUS.

Received 12th November, 1931.

This work was undertaken as a continuation of an investigation of the photochemical reaction of ammonia and amines with ethylene, in which an induced polymerisation of ethylene was observed.¹ It was suggested that this was initiated by hydrogen atoms formed in the ammonia decomposition, or by free alkyl radicals from the amines. Berthelot studied the photo-reaction between carbon monoxide and ammonia, and concluded that formamide was the primary reaction product, but that it underwent a secondary decomposition.² This result is of considerable theoretical interest, for the absorption spectrum of ammonia is of the predissociation type,³ which is interpreted as meaning that the ammonia molecule, after absorbing light, decomposes within a time which is short compared with the time between consecutive collisions at atmospheric pressure. If all of the ammonia molecules absorbing light behave in this way, formamide must result from the collision of CO molecules with the decomposition products, which are probably H and NH₂. If, on the other hand, the excited ammonia molecule has a normal existence, then formamide might result directly from its collision with carbon monoxide.

The results presented below represent a repetition and amplification of Berthelot's work. The investigation has been extended by a comparison of the ammonia decomposition rate with and without carbon monoxide present, and also by observations on the photochemical reaction between carbon monoxide and amines.

Experimental.

Carbon monoxide was generated by the action of sulphuric acid on formic acid, and was dried by sulphuric acid. Ammonia was prepared by fractionally distilling the commercial gas, whilst the amines were made from the hydrochlorides of the bases, and fractionated. Gas mixtures were made up in the evacuated quartz reaction vessel by admitting each gas in turn from its storage globe up to the required pressure, measured with a constant volume mercury manometer. Reaction mixtures were illuminated with the unfiltered light of a hot mercury arc of the vertical type, operated at an amperage of 2.3 to 2.6, and with a voltage drop of 55 to 65 volts across it. Light of wave-length less than 2260 Å. is absorbed by ammonia, whilst carbon monoxide⁴ absorbs only below λ 1800 Å. To obtain a light intensity sufficiently great to give a moderate

¹ Taylor and Emeléus, *J.A.C.S.*, **53**, 562, 1931; **53**, 3770, 1931.

² Berthelot and Gaudechon, *C.R.*, **155**, 207, 1912.

³ Bonhoeffer and Farkas, *Z. physikal. chem.*, **134**, 337, 1928.

⁴ Leifson, *Astrophys. J.*, **63**, 73, 1926.

90 PHOTOCHEMICAL REACTION OF CARBON MONOXIDE

reaction rate, all of the experiments on the carbon monoxide—ammonia reaction were made with the arc at 1 to 2 cms. from the surface of the reaction vessel, corresponding to a temperature of the latter of 100° to 150°. All pressure measurements were made after illumination with the quartz bulb in a water bath at a definite temperature, and all gas quantities are recorded in terms of the pressure in the constant volume reaction system.

The Reaction between Carbon Monoxide and Ammonia.

On illuminating under the above conditions the total pressure of the gas mixture decreased slowly (1 to 2 cms. per hour) and a brownish semi-liquid film formed on the walls of the bulb, retarding the reaction as it accumulated. At the end of an experiment the bulb was cooled in liquid air and the residual non-condensable gas pumped off and analysed. During the pumping, condensable gas from the dead space of the apparatus was frozen out in a small U-tube cooled in liquid air, and was returned to the reaction vessel before measuring the residual pressure in the latter. The non-condensable gas consisted mainly of carbon monoxide; a very small residue not absorbed in ammoniacal cuprous chloride was taken to be a mixture of nitrogen and hydrogen formed in the normal decomposition of part of the ammonia. It represented only 2 to 6 per cent. of the total ammonia which reacted. The pressure of this gas is recorded in Table I. under $p_{(N_2 + H_2)}$. The values of Δp_{CO} represent the amount of carbon monoxide which reacted. The residual condensable gas was found to be pure ammonia; it was quantitatively absorbed on distilling in vacuum into 5 per cent. sulphuric acid, and had a vapour pressure curve between -80° and -35° corresponding closely with that of a sample of pure ammonia. From this residual pressure the pressure of the ammonia which had reacted was calculated. The results of these experiments are recorded in Table I.

TABLE I.

	p_{NH_3} , cms.	p_{CO} , cms.	Dist. of Arc, cms.	Time (hours).	Δp_{NH_3} , cms.	Δp_{CO} , cms.	$\frac{\Delta p_{NH_3}}{\Delta p_{CO}}$	$p_{(N_2 + H_2)}$, cms.
1	12.99	15.56	2.0	16	-3.90	-3.72	1.05	0.46
2	13.09	24.60	1.5	15.5	-7.20	-7.41	0.97	0.41
3	19.24	17.48	1.5	18	-4.72	-4.66	1.01	—
4	15.01	14.24	1.5	2	-1.57	-1.58	1.00	—
5	24.09	24.97	1.0	15.5	-7.93	-7.86	1.01	0.25
6	30.57	26.34	1.0	14	-7.46	-6.88	1.08	0.20
7	3.93	19.19	1.5	10.5	-2.30	-4.81	0.48	—
8	3.74	22.48	1.0	3.5	-2.64	-3.66	0.72	—

In the table the value of $\frac{\Delta p_{NH_3}}{\Delta p_{CO}}$ is very close to unity in Expts. 1 to 6. This agrees with Berthelot's result that equal volumes of the two gases take part in the photo-reaction, and the equation for the reaction may be written



The deposit formed in small amounts on the walls of the reaction vessel was soluble in water, giving a brown solution which was free from

formaldehyde, hexamethylenetetramine, glyoxal, cyanide, and ammonium salts. On boiling with dilute alkali ammonia was evolved freely, indicating that an amide was present, and the neutral solution prepared after hydrolysis reduced silver nitrate readily on warming, but gave negative tests for oxalic acid. This evidence is consistent with the presence of formamide in the residue, although attempts to isolate a specimen of the pure amide by distillation in high vacuum, and to identify it by its physical properties were unsuccessful.

Formamide itself was shown to decompose photochemically by illuminating about 1 c.c. of the pure liquid in a quartz bulb, when a mixture of solid and liquid products was deposited on the walls, and a small amount of gas (30 per cent. condensable in liquid air) was evolved. When the products of the ammonia-carbon monoxide reaction were freed from unchanged reactants and the illumination was continued, a slow gas evolution was observed. Moreover, on illuminating carbon monoxide with formamide the pressure was found to decrease slowly, showing that the amide was capable of reacting photochemically with carbon monoxide. This will probably explain the low

value of the ratio $\frac{\Delta p_{\text{NH}_3}}{\Delta p_{\text{CO}}}$ observed in Expts. 7 and 8 (Table I.). In these two runs there was a deficit of ammonia, and the carbon monoxide apparently continued to react with the main reaction product when the ammonia pressure had become low.

Rate of Reaction of Ammonia with and without Carbon Monoxide Present.

A series of experiments was next made to determine if ammonia decomposed at its normal rate in presence of carbon monoxide. Due to the retardation of the reaction by its products, it was necessary to make these observations over short periods. The arc was set up at a definite distance from the reaction bulb, which contained a known pressure of ammonia, and the amount of ammonia decomposed in a definite time was determined from the pressure change (measurements being made after illuminating, with the quartz bulb in a water bath at room temperatures). The ammonia was then pumped out and an ammonia-carbon monoxide mixture substituted, the amount of ammonia decomposed being again determined for a short period of illumination by observing the pressure change ($= 2 \times p_{\text{NH}_3}$). Results obtained in this way are given in Table II.

The pressure of ammonia which reacted was taken as half the total pressure decrease in the carbon monoxide-ammonia mixture. Expts. 1, 2 and 3 were made with a narrow bulb (2.5 cms. diam.) and R , the ratio of the pressure of ammonia decomposed per hour with and without carbon monoxide had a value of approximately 2. This result was reproducible under these experimental conditions. The fourth group of runs was made with a bulb 4.5 cms. in diameter. The ammonia decomposition rate in the clean bulb was first measured, and then the rate of its disappearance in presence of carbon monoxide. R had a value of 1.8. Without cleaning the bulb the ammonia decomposition rate was re-measured, and was found to be reduced to less than half, corresponding to a value of R of 4.0. This must mean that the values of R observed are always too low, since reaction product will be deposited on the walls of the quartz bulb from the start of illumination in all of the experiments

TABLE II.

	p_{NH_3} , cms.	p_{CO} , cms.	Total Δp , cms.	Time (hours).	Δp_{NH_3} per hour, cms.	R .	Distance of Arc, cms.
1	19.57	21.71	-6.26	2	-1.56	2.1	1.0
	22.86	—	+2.26	3	-0.75	—	—
2	9.46	20.29	-2.92	1	-1.46	1.85	1.0
	23.40	—	+1.39	1.75	-0.79	—	—
3	14.88	14.06	-0.87	0.5	-0.87	2.0	1.0
	16.44	—	+0.43	1	-0.43	—	—
4	22.61	—	+0.73	1	-0.73	1.82	1.2
	22.33	23.34	-2.00	0.75	-1.33	—	—
	21.25	—	+0.33	1	-0.33	4.0	—
5	17.33	15.98	-2.20	1	-1.10	1.34	2.5
	17.77	—	+1.36	1.66	-0.82	—	—

with carbon monoxide present. This retardation is exaggerated in Expt. 5, in which the wider bulb was used (4.5 cms. diam.), the arc being set at 2.5 cms. from its surface. The wall of the bulb remained relatively cool, and the reaction product was deposited more readily, giving a value of R of only 1.3.

From these experiments it was concluded that the rate at which ammonia reacts on illumination in presence of carbon monoxide was of the order of twice its normal decomposition rate when illuminated alone. The experiments with and without carbon monoxide were carried out under approximately identical conditions, so that this result cannot be attributed to the influence of temperature on the quantum yield in the decomposition of ammonia, which was observed by Kuhn.⁵

Photochemical Reaction of Methylamine and Ethylamine with Carbon Monoxide.

The following experiments were made to determine if methylamine and ethylamine will react photochemically with carbon monoxide. The experimental method was the same as that already described. The amine-carbon monoxide mixture was illuminated in a quartz bulb heated in a furnace with a quartz window (6×2 cms.). During the reaction a brown deposit formed. The residual non-condensable gas was pumped off and the per cent. of carbon monoxide in it determined. The residue in the reaction bulb was distilled into 5 per cent. sulphuric acid to determine the amount of unchanged amine. The residual non-condensable gas other than carbon monoxide was taken to be a mixture of hydrogen, nitrogen, and methane. These results are found in Table III.

In a single experiment with ethylene, the following results were obtained. The composition of the original gas mixture was $p_{\text{C}_2\text{H}_5\text{NH}_2} = 20.18$ cms., $p_{\text{CO}} = 19.86$ cms. This was illuminated for twenty-four hours with the arc at 1.5 cms. from the reaction bulb, and gave a total pressure decrease of 2.60 cms., $\Delta p_{\text{C}_2\text{H}_5\text{NH}_2} = -12.60$ cms., $\Delta p_{\text{CO}} = -5.42$ cms., and $p_{\text{N}_2 + \text{H}_2 + \text{CH}_4} = 14.45$ cms.

⁵ Kuhn, *J. Chim. physique*, **23**, 521, 1926.

TABLE III.

	$p_{\text{CH}_3\text{NH}_2}$, cms.	p_{CO} , cms.	Δp in Reaction, cms.	$\Delta p_{\text{CH}_3\text{NH}_2}$, cms.	Δp_{CO} , cms.	$p_{(\text{N}_2 + \text{H}_2 + \text{CH}_4)}$, cms.	Conditions.
1	24.28	—	+2.23	-3.55	—	5.78	18 hrs. at 260°
2	24.80	23.59	+0.93	-3.52	-2.15	6.60	14 " " 260°
3	21.12	—	+1.29	-2.35	—	3.64	15 " " 125°
4	20.44	19.63	-2.04	-4.13	-4.04	6.13	64 " " 125°
5	17.14	18.23	-2.35	-3.45	-3.65	4.75	22 " " 125°

These results show definitely that methylamine and ethylamine react photochemically with carbon monoxide. The reaction differs from that for ammonia in that the quantity of non-condensable gas formed is approximately the same as in the decomposition of the amines alone. At 125° the amounts of methylamine and carbon monoxide reacting are almost equal, whilst at 260° there is a 1.6 : 1 ratio between them. In the single experiment with ethylamine the amount of amine decomposed was of the order of twice the carbon monoxide reacting. No definite information was obtained as to the nature of the products of these reactions, but it is of interest to record that in the reaction between methylamine and carbon monoxide the liquid product deposited on the walls of the reaction bulb had the smell usually associated with acetamide, and it is likely that this was formed as one of the primary products.

Discussion.

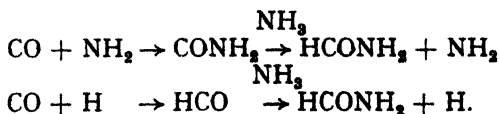
The experiments described support Berthelot's conclusion that carbon monoxide and ammonia react photochemically, giving formamide as the first product. Any mechanism put forward to explain the reaction must account both for the increased rate of reaction of ammonia in presence of carbon monoxide, and for the very small amount of its normal decomposition products which is formed.

There are two general methods by which the reaction might take place: either the ammonia molecule first decomposes and its decomposition products then react with carbon monoxide, or the excited ammonia molecule may react with carbon monoxide, giving a direct addition. The first view is favoured by the interpretation given at present to the absorption spectrum of ammonia, which is of the pre-dissociation type. According to Bonhoeffer and Farkas³ ammonia molecules, after absorbing light, decompose without making a collision. The decomposition products are probably H and NH₂ (or possibly NH and H₂, as suggested by Gedye⁶). The low quantum yield in the ammonia decomposition (= 0.25) must then be attributed to a partial recombination. There appears to be no simple mechanism by which NH₂ and H can react exclusively with carbon monoxide to yield for-

⁶ Gedye, *Trans. Faraday Soc.*, **27**, 474, 1931.

94 PHOTOCHEMICAL REACTION OF CARBON MONOXIDE

amide and as little as 5 per cent. of the normal decomposition products unless one introduces a chain of reactions such as



Such a mechanism would account for the increased rate of reaction of ammonia and for the production of such a small amount of nitrogen and hydrogen, but the 1 : 1 reaction ratio between ammonia and carbon monoxide would no longer hold unless the chain breaking reaction is a recombination of NH_2 and H.

If a certain proportion of the excited ammonia molecules have a normal life, or if a reactive ammonia molecule is produced by the recombination of the products of dissociation, as postulated by Bonhoeffer to explain the low quantum yield in the decomposition of ammonia, then formamide might be produced directly by the reaction $\text{NH}_3' + \text{CO} = \text{HCONH}_2$. A mechanism of this type seems more probable than one involving the dissociation products. It accounts for the increased rate of decomposition of ammonia, since the excited ammonia molecule, which normally would simply lose its energy, has the alternative of reacting with carbon monoxide. On this view the molecules of ammonia which dissociate and do not recombine may be those responsible for the formation of the small amount of free nitrogen and hydrogen observed, though this argument cannot be rigorously applied until more is known of the stages by which the normal decomposition of ammonia occurs, and of possible side reactions. In the case of the photochemical reaction between ethylene and ammonia the rate of decomposition of ammonia was unaltered by the presence of ethylene. This harmonises with the view put forward, since the polymerisation of ethylene was considered as being initiated by hydrogen atoms formed in the photo-decomposition of ammonia, and excited molecules played no part. It may be possible, however, to find other photochemical reactions of ammonia in which the excited ammonia molecule takes part, and in which an increased quantum yield is observed. Such evidence would support the tentative explanation put forward in the present case.

Summary.

1. The photochemical reaction of ammonia with carbon monoxide yields formamide as a primary product, which then undergoes secondary reactions.
2. Less than 5 per cent. of the ammonia reacting yields the normal decomposition products, nitrogen and hydrogen.
3. The rate of ammonia decomposition is approximately doubled in presence of carbon monoxide.
4. Possible mechanisms for the reaction are discussed.

The author wishes to express his gratitude to Professor H. S. Taylor for his interest and advice during this research. It has been carried out in the Frick Chemical Laboratory of Princeton University during the tenure of a Commonwealth Fund Fellowship.

*Imperial College of Science and Technology,
London, S.W.7.*

THE VAPOUR PRESSURES OF BINARY MIXTURES.

BY ALFRED W. PORTER, D.Sc., F.R.S.

Received 27th November, 1931.

In a paper read before the Faraday Society in 1919,¹ I called renewed attention to the Duhem-Margules equation for the vapour pressures of binary mixtures, and followed it up by other papers on the same subject.

In the first paper, I took a simple form of the equation, according to which $\log \frac{\pi_1}{\Pi_1 \mu_1} = \beta \mu_2^2$, where μ_1, μ_2 are the molar fraction of the two components, π_1 and Π_1 the vapour pressures of No. 1 for the solution and in the pure state. This was applied in particular to experimental results obtained by Sameshima² for acetone and ethyl ether mixtures.

In recent papers, Professor Bancroft and his co-workers have put forward approximate formulæ in various forms, one of which³ is equivalent to $\pi_1/\Pi_1 = \mu_1^a$. This gives values for the vapour pressures if appropriate values of a are chosen which are somewhat remarkably very similar to those obtained by the formula given by me above. If the object is to obtain approximate values of the vapour pressures for different molar fractions of the components, Professor Bancroft's formula may be sufficiently accurate. But he is specially concerned with the deviations from Raoult's Law, especially for fairly dilute solutions, and it is precisely for such dilute solutions that his formula is most unsatisfactory.

In preparing my first paper, it was noticed by me that very fair agreement was obtained by either of the two formulæ referred to here. This gave one considerable anxiety, since it seemed possible to fit the experimental values to two different equations from which very different values would be obtained for the deviations from Raoult's law. The degree of correspondence can be exhibited by placing side by side Sameshima's experimental values for the vapour pressure of acetone in the mixture and those calculated by Professor Bancroft and myself.[†]

It will be observed that while I have taken the value for $\mu_1 = 1$ as the standard, Professor Bancroft appears to have chosen his constant a so as to fit the points for μ_1 nearly equal to unity, while the value calculated for $\mu_1 = 1$ is considerably less than the experimental value. This is an important fact to which further reference is made later.

The most obvious remark on this duality in possible representations is that both equations automatically fit the experiments at $\mu_1 = 0$, and at $\mu_1 = 1$ (or at some point near it) by a choice of Π_1 , and at some intermediate point by a choice of a in the one case and of β in the other. If the curve has not much curvature, there may be fair correspondence throughout. There are essential differences, however, between the two calculated curves. With Professor Bancroft's formula there is no point of inflexion on the vapour pressure curve, while my formula indicates

¹ *Trans. Far. Soc.*, **15**, 1920.

² *J. Physic Chem.*, **35**, 3181, 1931.

³ *Amer. J. Sci.*, **40**, 1482, 1918.

[†] See next page.

ACETONE AND ETHYL-ETHER.

μ_1 .	Experimental π_1 .	Calculated.	
		Bancroft.	Porter.
0.03837	21.8	27.7	21.7
.1327	66.2	66.3	65.5
.2509	106.7	104.4	107.4
.3454	132.4	131.3	134.2
.4958	167.5	169.9	169.2
.6507	201.2	201.3	201.4
.7047	213.7	218.4	212.4
.8381	243.1	247.2	241.1
.9337	266.8	266.8	265.3
.9528	270.7	270.9	269.6
.9799	276.6	276.4	277.1
1.0000	282.7	280.5	282.7

such a point. It is important to observe that such a point is clearly indicated by Sameshima's experimental values. It should be further remarked that it is at the two ends of the curve that Professor Bancroft's fit to the experiments is most imperfect. However, a glance at the table shows that there is very fair agreement along part of the curve, and for some purposes it may be sufficient.

Owing to this duality of possible representation, I kept my first paper back for some time. It was not until I discovered a satisfactory way of discriminating between the formulæ that I ultimately published.

Both formulæ are special cases of Margules' general theorem. Both are included in the form,

$$y = \log_e \frac{\pi_1}{\Pi_1 \mu_1} = (a - 1) \log_e \mu_1 + \beta \mu_2^2.$$

At $\mu_1 = 1$ both sides equal zero. At this point the slope of the curve of y (obtained by differentiating with respect to μ_1) is $a - 1$, and is *therefore independent of β* . From an examination of this slope, therefore, the value of a can be determined. Such curves are plotted in Fig. 1 for acetone-ether (Sameshima) and for alcohol-water (Dobson). In both cases the curve starts out *horizontally* from $\mu_1 = 1$. Professor Bancroft takes the value of $a - 1$ as .4 for acetone-ether. The curve shows that this is an *impossible* value, whether we neglect the β term or not. I have indicated by an arrow the initial slope according to Professor Bancroft's value of a for acetone-ether. It was the observation of this that convinced me in 1920 that the value of a is in such a case sensibly unity, and to explain the character of the y curve it is necessary to include at least one extra term (with coefficient β) satisfying the Margules general form. If a is taken greater than unity and Professor Bancroft's formula is adjusted to neighbouring points, then the value of y at $\mu_1 = 1$ becomes negative; this means that the value of π_1 at $\mu_1 = 1$ must be taken at less than its experimental value. This accounts for the necessity in Professor Bancroft's calculated values of taking it as 280.5 instead of 282.7.

For the alcohol-water curve a is also unity.

It should be observed that the value of β can be simply read off the y -curve as the ordinate at $\mu_1 = 0$ (because then $\mu_2 = 1$) provided that

logarithms to base e have been used. The continuous lines on Fig. 1 represent the values according to my formula, employing logarithms to base 10—the circles are the experimental points. Professor Bancroft's value at $\mu_1 = .03837$ gives a value of γ_- equal to $4/3$ of the experimental value for acetone-ether and it would therefore fall well off the diagram.

When we pass from simple mixtures, *i.e.*, cases in which chemical

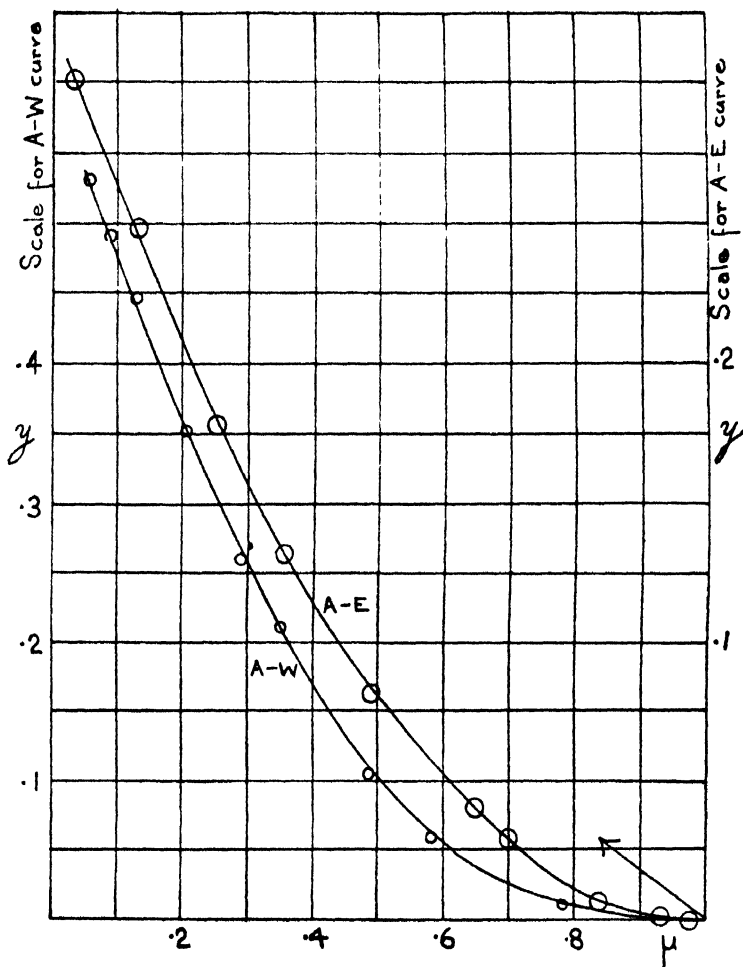


FIG. 1.

action is either absent or insignificant, to cases of solution of salts, a in general has a value different from unity, and may be positive or negative, and it is usually necessary to include more than two Margules' terms. Nothing further need be said here concerning the more general problem. I have dealt with it in a succession of papers.⁴

⁴ *Trans. Farad. Soc.*, **24**, 343, 405, 1928; see also U. Nakaya, *Ibid.* **24**, 543, 1928.

THERMODYNAMICS APPLIED TO THE IRON-CARBON SYSTEM.

BY F. H. JEFFERY.

Received 14th December, 1931.

In the volume of the Transactions for December, 1931,¹ there appeared two papers by Yap, Chu-Phay and also a paper by the author dealing with this subject. Yap, Chu-Phay often differs from the author alike in method and in results. The principal differences are:—

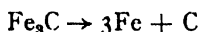
(1) He considers that the liquid phase in equilibrium with austenite is a solution of Fe_3C in iron, the author finds that it is a solution of C in iron.

(2) He considers that austenite is a solid solution of Fe_3C in γFe below 1020° but of C in γFe above this temperature; the author finds no such transition.

(3) For the liquidus from 1487° to 1130° he used the work of Ruer and Goerens and he drew the corresponding solidus rectilinearly, the author used that of Gutowski for both liquidus and solidus; for the austenite-cementite boundary he used results which he had derived from the dilatometric data of Sato, the author used the work of Tschischewsky and Schulgin.

(1)

If the liquid solution in equilibrium with austenite is a solution of Fe_3C in iron, and austenite is a solid solution of C in γFe , the reaction taking place when solid is formed from the liquid is



$$\nu_0 \log (1 - n) + \nu_1 \log n + \nu_0' \log (1 - n') + \nu_1' \log n' = \log K$$

where n is the molal fraction of Fe_3C in the liquid solution and n' the molal fraction of C in the solid solution

also $\nu_0 = 0, \nu_1 = -1, \nu_0' = 3, \nu_1' = 1$

and
$$\frac{\partial}{\partial \theta} \log K = \frac{-\lambda}{R\theta^2},$$

hence
$$\frac{\partial}{\partial \left(\frac{1}{\theta}\right)} \{ \log n' + 3 \log (1 - n') - \log n \} = \frac{\lambda}{R} \quad . \quad . \quad (i)$$

for dilute solutions, and if λ , the molal heat of the total reaction involved in the formation of the solid solution from the liquid solution, be sensibly constant for the range of concentration and temperature examined, the equation can be integrated giving

$$\log n' + 3 \log (1 - n') - \log n = \frac{\lambda}{R\theta} + \text{constant},$$

hence the sum of the logarithmic terms is a linear function of $1/\theta$ provided the molecular constitutions have been selected so as to satisfy the phase boundaries.

If the liquid solution is a solution of C in iron and austenite a solid solution of C in γFe

$$\frac{\partial}{\partial\left(\frac{1}{\theta}\right)}\{\log(1-n') - \log(1-n)\} = \frac{\lambda}{R} \quad . \quad . \quad . \quad (ii)$$

where n, n' are the molal fractions of C.

With restrictions similar to those given above

$$\log(1-n') - \log(1-n) = \frac{\lambda}{R\theta} + \text{constant}.$$

An equation of the same form as that of (ii) is applicable to such a system as a liquid solution and a solid solution of Fe_3C in iron as solvent in equilibrium with each other, were such to exist, but it is not applicable to a system in which the solute in the liquid solution is different from the solute in the solid solution: and any equation derived from it or any calculation based on it is equally inapplicable to such a system. Yap, Chu-Phay appears to have used an equation of the form of (ii) and to have deduced from it the existence of the system to which equation (i) applies.

Yap, Chu-Phay considers that the liquid phase above the isothermal at 1487° is a solution of C in iron, but that below this isothermal the liquid is a solution of Fe_3C in iron. This leads to the remarkable conclusion that the compound Fe_3C in liquid solution with one of its constituent elements, iron abruptly, and completely, dissociates at the temperature 1487° .

(2)

Yap, Chu-Phay considers that the austenite-cementite boundary is very nearly rectilinear; that the eutectoid isothermal is at 720°C ., the eutectoid composition being 0.80 per cent. carbon; and that this boundary meets the eutectic isothermal at 1.68 per cent. carbon.

The author in his paper showed that for the austenite-cementite boundary, if austenite is a solid solution of C in γFe , an equation of the form

$$-\frac{\partial}{\partial\left(\frac{1}{\theta}\right)}\{3\log(1-n) + \log n\} = \frac{\lambda}{R} \quad . \quad . \quad . \quad (iii)$$

is applicable; but that if austenite is a solid solution of Fe_3C in γFe the form of the equation must be

$$-\frac{\partial}{\partial\left(\frac{1}{\theta}\right)}\log n = \frac{\lambda}{R} \quad . \quad . \quad . \quad . \quad (iv)$$

Yap, Chu-Phay appears to have used an equation of the form (iv) for his line from 720° to 1130° .

He considers that there is a "point-saillant" on this boundary line at 1020° , and that above 1020° the constitution of austenite is C in γFe , but below, Fe_3C in γFe .

The author has calculated the molal fraction of carbon in the alloys which Yap, Chu-Phay has used for his line. The results are as follows :—

	Per Cent. Carbon.	n.
720° C.	0.80	3.61×10^{-2}
780	0.92	4.14
856	1.07	4.79
870	1.12	5.00
925	1.24	5.52
968	1.33	5.90
1070	1.55	6.82
1130	1.68	7.36

It will be found that if the temperature be plotted as a function of n the points will lie very well on a straight line through the second point and the last. There is no indication of a "point-saillant" at 1020°.

If austenite is a solid solution of C in γFe an equation of the form of equation (iv) is inapplicable to the boundary above 1020°, while if austenite is a solution of Fe_3C in γFe from 720° to 1020° it must be so up to 1130° in the absence of a transition line. This latter result is incompatible with the result which Yap, Chu-Phay obtained by his method of considering the solidus and liquidus from 1130° to 1487° unless it be assumed that there is a transition line at 1130°; but of this there is no proof.

(3)

Undoubtedly the choice of correct phase boundaries from which to form the thermal equilibrium diagram is of fundamental importance. Such a choice is difficult for the iron-carbon system, the results of various investigators not being consistent with each other. If the boundaries are substantially correct, thermodynamic equations can be found which satisfy the boundary conditions: and the molecular constitutions of the various phases so found are compatible with each other. In the author's work ten boundaries were involved, they gave consistent results: eight of these were involved in obtaining the constitution of austenite.

The question arises whether if one set of boundaries gives consistent results it would be possible to choose another set from the work of other investigators which would give equally consistent results. The author thinks that the greater the number of boundaries involved the less probable it is that a second consistent set could be found. Nonetheless inasmuch as the thermodynamic equations apply to dilute solutions, it is quite possible that further experimental work might make modifications of curvature at concentrations beyond those to which the equations can be applied, though not thereby automatically destroying the validity of the results based on these equations: it is possible that such may prove to be the case for the solidus and liquidus between 1130° and 1487°.

*The Goldsmiths' Metallurgical Laboratory,
Cambridge.*

THE BROMINE-BROMIDE-TRIBROMIDE EQUILIBRIUM.

BY ROBERT OWEN GRIFFITH, ANDREW McKEOWN, AND
ALBERT GORDON WINN.

Received 15th December, 1931.

In connection with the study of the thermal reaction between bromine and oxalates (see the following paper), a rather more detailed knowledge of the equilibrium constant (K_3) of the equilibrium $\text{Br}_2 + \text{Br}^- \rightleftharpoons \text{Br}_3^-$ than that hitherto available was desired. Previous work on this equilibrium may briefly be summarised. It was first studied by Jakowkin,¹ using the well-known partition method with carbon tetrachloride as the second phase. Later, Worley² investigated the equilibrium by allowing two aqueous solutions, the one containing bromine, the other bromine and potassium bromide, to come to equilibrium *via* the vapour phase, and then analysing the two solutions. Again, Jones and Hartmann³ combining Jakowkin's method with measurements of electrical conductivity, carried out an elaborate study of the tribromide equilibrium at 0°. In their calculations of the equilibrium constant they made allowance for (a) the hydrolysis of bromine and (b) the formation of pentabromide (Br_5^-). In each of these investigations most of the data refer to solutions of high bromine content, in which, owing to allowance having to be made for pentabromide formation and also to possible deviations from the laws of dilute solution, the interpretation of results becomes needlessly complex and to some extent uncertain.

Lewis and Storch⁴ showed that the partial pressures of bromine above solutions of bromine in carbon tetrachloride are proportional to concentration up to about 0.25*M*. (This corresponds to a concentration of free bromine in an aqueous layer in equilibrium with the carbon tetrachloride layer of about 0.01*M*.) Above this concentration deviations from Henry's Law are to be expected. They also determined the value of K_3 in presence of HBr at 25° by the Jakowkin method. In measuring the partition coefficient of bromine between water and carbon tetrachloride they made the aqueous phase *N*/1000 with respect to H_2SO_4 in order to cut down hydrolysis of the bromine. Lewis and Randall⁵ have recalculated some of Jakowkin's results obtained with KBr and weak bromine solutions, and Linhart⁶ has attempted to correct Worley's data (relating to solutions strong in bromine) by making allowance for pentabromide formation. Finally, Sherrill and Izard⁷ have carried out a series of measurements of K_3 in the presence of HBr. They found that the values of this equilibrium constant (defined as $K_3 = [\text{Br}_2][\text{Br}^-]/[\text{Br}_3^-]$) decreases with increasing concentration of bromide, a variation which

¹ Jakowkin, *Z. physikal. Chem.*, **18**, 583, 1895; **20**, 19, 1896.

² Worley, *J.C.S.*, **87**, 1107, 1905.

³ Jones and Hartmann, *Trans. Amer. Electrochem. Soc.*, **30**, 295, 1916.

⁴ Lewis and Storch, *J. Amer. Chem. Soc.*, **39**, 2544, 1917.

⁵ Lewis and Randall, *J. Amer. Chem. Soc.*, **38**, 2348, 1916.

⁶ Linhart, *J. Amer. Chem. Soc.*, **40**, 158, 1918.

⁷ Sherrill and Izard, *J. Amer. Chem. Soc.*, **50**, 1665, 1928.

they were the first to note. In Table I. the results of these previous investigations are summarised.

TABLE I.—VALUES OF THE EQUILIBRIUM CONSTANT K_3 .

Author.	Bromide.	Temperature.	K_3 .
Jones and Hartmann	KBr	0°	0.051
Lewis and Storch	HBr	25°	0.061
Jakowkin (calculated by Lewis and Randall)	KBr	25°	0.062
Worley (calculated by Linhart) . .	KBr	26.5°	0.063
Worley	KBr	32.5°	0.065
Sherrill and Izard	HBr	25°	0.057–0.060

We have carried out fresh determinations of the equilibrium at the two temperatures 16.5° and 21.5°, using HBr, NaBr, KBr and LiBr, varying the concentration of electrolyte between 0.03 and 0.75 *N* and keeping the concentration of free bromine below 0.01 *M*.

Experimental.

The method of Jakowkin was adopted, with carbon tetrachloride as the second solvent. Two preparations of bromine were used, the one from Kahlbaum, the other sample purified by the method of A. Scott.⁸ Also two preparations of CCl_4 were employed. The first of these was an A.R. grade sample which had been specially purified for photochemical work by refluxing with pure chlorine in an all-glass apparatus, washing with Na_2CO_3 solution, drying over Na_2CO_3 and then over Na, and finally fractionating. The second preparation, of the same origin, was subjected to similar treatment, with the difference that the refluxing was carried out with bromine instead of with chlorine and that the final drying with Na was omitted. The bromides were Kahlbaum or Merck preparations and were found to be free from impurities which react with bromine.

In all cases at least forty-eight hours was allowed for attainment of equilibrium between the aqueous phase and the carbon tetrachloride phase. The bromine content of each layer was determined by pipetting off samples, running into excess of sodium arsenite solution, and back titrating with iodine.

In determining the distribution coefficient of bromine between CCl_4 and water in the absence of added bromides, the method of Lewis and Storch for limiting the hydrolysis of bromine in the aqueous phase was used, *i.e.*, the aqueous phase was made *N*/1000 with respect to H_2SO_4 . Table II. gives the results of distribution measurements using this procedure. The effect of hydrolysis of bromine in the aqueous layer is shown in the results of Table III., relating to experiments with much weaker bromine solutions in absence of added acid. In these and the following tables, concentrations are expressed in moles per litre, and *D* represents the ratio
$$\frac{\text{concentration of Br}_2 \text{ in } \text{CCl}_4}{\text{concentration of Br}_2 \text{ in } \text{H}_2\text{O}}$$

⁸ A. Scott, *J.C.S.*, 103, 847, 1913.

TABLE II.

	$t = 21.5^\circ$				$t = 16.5^\circ$	
$[\text{Br}_2]_{\text{CCl}_4}$	0.1880	0.1881	0.1775	0.370	0.1843	0.1838
$[\text{Br}_2]_{\text{H}_2\text{O}}$	0.00682	0.00682	0.00646	0.01328	0.00700	0.00700
D	27.6	27.6	27.5	27.8	26.3	26.3

TABLE III.

	$t = 16.5^\circ$				
$[\text{Br}_2]_{\text{CCl}_4}$	0.1272	0.0748	0.03755	0.02360	0.01653
$[\text{Br}_2]_{\text{H}_2\text{O}}$	0.004950	0.002939	0.001490	0.000985	0.000698
D	25.8	25.5	25.2	24.0	23.7

Before presenting the results of the distribution experiments with solutions containing bromide, it is convenient first to deal with the method of calculating K_3 from these data. Previous authors have proceeded as follows.

Let ΣBr_2 be the concentration of titratable bromine in the aqueous layer; $[\text{Br}_2]_{\text{CCl}_4}$ be the concentration of bromine in the CCl_4 layer; and ΣBr^- be the total concentration of bromide (*i.e.*, $[\text{Br}^-] + [\text{Br}_3^-]$) in the aqueous layer.

$$\text{Then } [\text{Br}_2]_{\text{H}_2\text{O}} = [\text{Br}_2]_{\text{CCl}_4}/D \quad (1)$$

$$[\text{Br}_3^-] = \Sigma\text{Br}_2 - [\text{Br}_2]_{\text{CCl}_4}/D \quad (2)$$

$$\text{and } [\text{Br}^-] = \Sigma\text{Br}^- - \Sigma\text{Br}_2 + [\text{Br}_2]_{\text{CCl}_4}/D \quad (3)$$

From these equations, K_3 is calculated.

Equation (1), however, is not strictly correct, since the expression $[\text{Br}_2]_{\text{CCl}_4}/D$ is not a measure of the concentration of Br_2 in the aqueous layer, but rather of its activity. In equations (2) and (3), therefore, an activity term is being subtracted from a concentration term, and the resulting constant, as ordinarily calculated, is neither in terms of activities nor of concentrations. In order to obtain correct values of K_3 (in terms of concentrations) allowance must be made for variations in the activity coefficient of bromine. As regards bromine in pure aqueous solution, it follows from Winkler's⁹ measurements of vapour pressure and from Lewis and Randall's⁵ determinations of the partial pressure of bromine above solutions in CCl_4 that for dilute solutions the activity of bromine is proportional to its concentration. When, however, the bromine is dissolved in aqueous salt solutions considerable variations in its activity coefficient (γ) are to be anticipated. The effect of salts on the activity coefficients of dissolved non-electrolytes has been discussed by Randall and Failey.¹⁰ From a survey of the available data on the solubilities of various gases (non-electrolytes) in salt solutions, they show

⁹ Winkler, *Chem. Zeit.*, **23**, 678, 1899.

¹⁰ Randall and Failey, *Chem. Reviews*, **4**, 271, 285, 291, 1927.

104 THE BROMINE-BROMIDE-TRIBROMIDE EQUILIBRIUM

that the ratio $(\log_{10} \gamma)/\mu$, where μ is the ionic strength of the solution, is approximately constant for a given non-electrolyte and a given salt.

Clearly, what is required in the present instance is the effect of bromides on the activity of bromine, but, on account of the formation

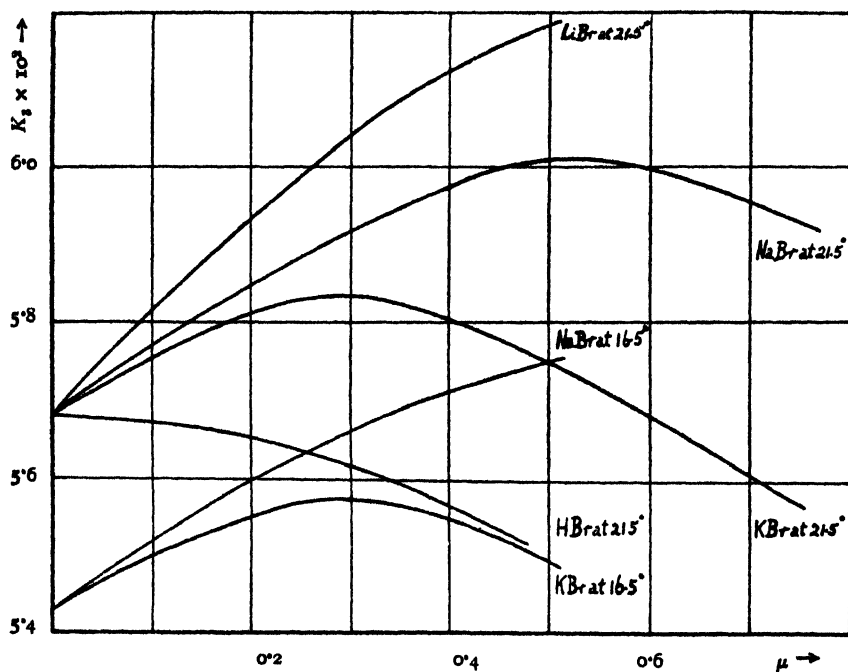


FIG. 1.

of tribromide ion this cannot be determined directly. Yet, from Randall and Failey's data an approximately correct estimate of this effect may be obtained. From these authors' tables we extract the figures given in Table IV.

TABLE IV.—ACTIVITY COEFFICIENTS OF NON-ELECTROLYTES IN SALT SOLUTIONS.

(AFTER RANDALL AND FAILEY.)

Non-electrolyte.	Salt.	$\log_{10} \gamma/\mu$.	Ratios.
I_2	Na_2SO_4	0.109	—
N_2O	Na_2SO_4	0.110	} $0.110/0.091 = 1.21$
N_2O	NaBr	0.091	
N_2O	KBr	0.061	} $0.110/0.061 = 1.81$
C_2H_2	Na_2SO_4	0.098	
C_2H_2	NaBr	0.077	} $0.098/0.077 = 1.27$
C_2H_2	KBr	0.048	
			} $0.098/0.048 = 2.04$

We have supplemented these data by determining the effect of Na_2SO_4 on the activity of Br_2 , by finding the partition coefficient at 21.5° between CCl_4 and an aqueous solution of Na_2SO_4 of concentration $M/6$ ($\mu = 0.5$). In this case we find $D = 31.3$; hence γ_{Br_2} in $M/6 Na_2SO_4 = 31.3/27.5 =$

1.134 and $(\log \gamma_{\text{Br}_2})/\mu = 0.109$. Combining this figure with the ratios given in Table IV., we infer that :

For Br_2 in NaBr , $(\log \gamma)/\mu = 0.109/1.24 = 0.088$.

For Br_2 in KBr , $(\log \gamma)/\mu = 0.109/1.92 = 0.051$.*

These estimates are probably reasonably accurate; it is not so easy, however, to evaluate the effects of HBr and especially of LiBr on the

TABLE V.—VALUES OF THE EQUILIBRIUM CONSTANT K_2 .

$\Sigma \text{Br}^- = \mu$.	ΣBr_2 .	γ_{Br_2} .	$[\text{Br}^-]$.	$[\text{Br}_2^-]$.	$[\text{Br}_2]$.	K_2 .
KBr Solutions at 21.5°.						
0.7500	0.05150	1.105	0.7023	0.04772	0.003782	0.0557
0.5000	0.03911	1.070	0.4651	0.03483	0.004283	0.0572
0.5000	0.01074	1.070	0.4904	0.009611	0.001129	0.0576
0.2500	0.01059	1.035	0.2415	0.008530	0.002060	0.0583
0.1000	0.04618	1.014	0.07404	0.02596	0.02022	0.0576*
0.1000	0.03123	1.014	0.08166	0.01834	0.01289	0.0574*
0.1017	0.01497	1.014	0.09248	0.009219	0.005751	0.0577
0.1009	0.01266	1.014	0.09303	0.007868	0.004792	0.0567
0.1000	0.009919	1.014	0.09386	0.006141	0.003778	0.0577
0.1000	0.005356	1.014	0.09665	0.003352	0.002004	0.0578
0.06727	0.008375	1.009	0.06288	0.004386	0.003989	0.0572
0.03683	0.003467	1.005	0.03550	0.001332	0.002135	0.0569
HBr Solutions at 21.5°.						
0.4627	0.01127	1.021	0.4527	0.01004	0.001227	0.0553
0.1851	0.01109	1.008	0.1767	0.008401	0.002689	0.0566
0.04627	0.009961	1.002	0.04204	0.004233	0.005728	0.0569
NaBr Solutions at 21.5°.						
0.7500	0.05020	1.160	0.7037	0.04630	0.003899	0.0593
0.5000	0.01047	1.107	0.4907	0.009328	0.001142	0.0601
0.2000	0.01092	1.043	0.1916	0.008369	0.002551	0.0584
0.0500	0.00760	1.011	0.04659	0.003409	0.004191	0.0573
LiBr Solutions at 21.5°.						
0.5000	0.01078	1.065	0.4904	0.009574	0.001206	0.0618
0.2000	0.01120	1.026	0.1915	0.008550	0.002650	0.0593
0.0500	0.007597	1.007	0.04659	0.003409	0.004188	0.0572
KBr Solutions at 16.5°.						
0.5000	0.01107	1.070	0.4900	0.009952	0.001118	0.0550
0.2500	0.01118	1.035	0.2409	0.009078	0.002102	0.0557
0.1000	0.01039	1.014	0.09346	0.006540	0.003850	0.0550
0.1000	0.03277	1.014	0.08050	0.01950	0.01327	0.0548*
0.0500	0.01080	1.007	0.04508	0.004920	0.005880	0.0539
NaBr Solutions at 16.5°.						
0.5000	0.01081	1.107	0.4903	0.009678	0.001132	0.0574
0.2000	0.01139	1.043	0.1912	0.008810	0.002580	0.0560
0.0500	0.007980	1.011	0.04633	0.003665	0.004315	0.0548

* Justification of this procedure follows from the derivation of Debye and McAuley (*Physikal. Z.*, 26, 22, 1925) of the effect of electrolytes on the activity coefficients of non-electrolytes. See also Sherrill and Izard (*J. Amer. Chem. Soc.*, 53, 1667, 1931), who have applied a correction analogous to that attempted here to their data on the equilibrium $\text{Cl}_2 + \text{Cl}^- \rightleftharpoons \text{Cl}_2^-$.

activity of Br_2 . From Randall and Failey's data, it is found that $(\log \gamma)/\mu$ for non-electrolytes in HCl is in general about one-fifth that in NaCl. Assuming the same ratio for HBr and NaBr, we obtain $(\log \gamma)/\mu = 0.018$ for the effect of HBr on γ_{Br_2} . For Br_2 in LiBr, the admittedly uncertain value $(\log \gamma)/\mu = 0.042$ was chosen.

In Table V. are summarised our determinations of K_3 in presence of HBr, NaBr, KBr and LiBr at 21.5° and 16.5° . The values of γ_{Br_2} used in each case are given. The values of D employed were 27.5 for the experiments at 21.5° and 26.3 at 16.5° , except in the three asterisked cases, relating to experiments with a somewhat high content of free bromine. For these the value of D used was 27.8 at 21.5° and 26.6 at 16.5° . The values of K_3 given in the above Table are shown plotted against the ionic strength (μ) in Fig. 1.

Discussion of Results.

The following points call for comment :—

(a) From the results with 0.1 *N* KBr solutions at 21.5° , it is seen that a good constant K_3 is obtained with ΣBr_2 varying nine-fold, no correction for pentabromide formation having been applied. It would appear that for solutions of low bromine content such as here employed pentabromide formation is not appreciable; further, it is likely that previous estimates of its extent (in stronger Br_2 solutions) are too high.

(b) K_3 varies with ionic strength. In solutions of NaBr, KBr, and (probably) LiBr the constant at first increases, passes through a maximum in the neighbourhood 0.4–0.6 *N*, and then decreases. The salt effect is greatest in the case of LiBr, least for KBr.

(c) With HBr, K_3 falls with increasing μ . This is in agreement with the results of Sherill and Izard, though the magnitude of the fall we obtain is somewhat less than theirs.

(d) The values of K_3 here presented are slightly less than those of previous workers. This is due to the correction made here for the activity coefficient of bromine.

(e) The rise of K_3 with increasing μ in the cases of the alkali halides is somewhat unexpected. Thus with NaBr at 21.5° , K_3 rises from 0.0568 at $\mu = 0$ to 0.0601 at $\mu = 0.5$, a rise of about 5.8 per cent. Since, however, over the same range γ_{Br_2} increases by about 10.7 per cent., the function $\gamma_{\text{Br}_2} \cdot K_3 = a_{\text{Br}_2} \cdot \frac{[\text{Br}^-]}{[\text{Br}_3^-]} = \frac{a_{\text{Br}_2} \cdot a_{\text{Br}^-}}{a_{\text{Br}_3^-}} \cdot \frac{\gamma_{\text{Br}_2^-}}{\gamma_{\text{Br}^-}}$ is about 16.5 per cent. greater at $\mu = 0.5$ than at $\mu = 0$. Since by definition $\frac{a_{\text{Br}_2} \cdot a_{\text{Br}^-}}{a_{\text{Br}_3^-}}$

is constant, this means that the activity coefficient of the tribromide ion is approximately 16 per cent. greater than that of the bromide ion when the cation is Na^+ and the ionic strength 0.5. That this result is not occasioned by an incorrect assumption regarding the activity of bromine in solutions of NaBr may be demonstrated as follows. The constant K_3 was determined at 21.5° for a solution (A) which was 0.05*M* with respect to NaBr and 0.15*M* with respect to Na_2SO_4 , i.e., with a total ionic strength $\mu = 0.5$; the value obtained was $K_3 = 0.0575$. In the calculation the value $\gamma_{\text{Br}_2} = 1.134$ was that obtained (see above) in *M*/6 Na_2SO_4 solution for which also $\mu = 0.5$. Combining these values of K_3 and γ_{Br_2} , it follows that in solution (A) the ratio $\gamma_{\text{Br}_2^-}/\gamma_{\text{Br}^-}$ is approximately 15 per cent. greater than in a solution of zero ionic strength, in good agreement with the result for 0.5*M* NaBr solution. This con-

clusion is not in agreement with that reached by Lewis and Randall,¹¹ who postulated that the activity coefficient of tribromide ion is less than that of the bromide ion.

We wish to thank the Department of Scientific and Industrial Research for a grant to one of us (A. G. W.) while this work was in progress. We are also indebted to Imperial Chemical Industries, Ltd., for a grant defraying part of the cost of this investigation.

*Muspratt Laboratory of Physical and Electrochemistry,
University of Liverpool.*

¹¹ Lewis and Randall, *Thermodynamics*, p. 520.

THE KINETICS OF THE BROMINE-OXALATE REACTION.

BY ROBERT OWEN GRIFFITH, ANDREW McKEOWN, AND
ALBERT GORDON WINN.

Received 15th December, 1931.

As a preliminary to a study of the photochemical oxidation by bromine of oxalic acid and various oxalates, it was considered desirable to investigate in some detail the corresponding thermal reaction over the whole range of possible oxalate mixtures from oxalic acid on the one hand to neutral oxalate on the other.

The thermal oxidation of oxalic acid by bromine has been studied by Roloff,¹ who found the reaction to be strongly retarded by hydrogen ion and also by bromide ion, and who consequently presumed that reaction occurs only between the bromine molecule and the oxalate ($C_2O_4^{--}$) ion. Addition of bromide diminishes the concentration of free bromine in the reaction mixture by the formation of tribromide, whilst addition of strong acids reduces the concentration of the $C_2O_4^{--}$ ion by suppressing both stages of the dissociation of the oxalic acid. In accord with this hypothesis, the bimolecular constants of Roloff were found to fall considerably during each experiment, following the increased acidity and the increased bromide ion concentration of the system as reaction proceeds:



Berthoud and Bellenot² have studied the action of bromine on neutral potassium oxalate. Primarily interested in the photochemical reaction, they have given the results of only a few experiments on the thermal process, all carried out in a region of high ionic strength, from 1.5 to 2.5, of the reaction mixture. In the presence of considerable excess of potassium oxalate and of potassium bromide the reaction was found to be unimolecular with respect to bromine, the unimolecular constant being proportional to the concentration of oxalate and inversely

¹ Roloff, *Z. physikal. Chem.*, **13**, 346, 1894.

² Berthoud and Bellenot, *J. Chim. physique*, **21**, 308, 1924.

proportional to that of bromide. The inferred mechanism is a reaction between the bromine molecule and the oxalate ion, identical with that of Roloff. The temperature coefficient of the process was found to be abnormally high, namely 5.99 between 0° and 11.5° C.

A more detailed study of the oxidation by bromine of oxalic acid and also of acid-oxalates has been carried out by Józefowicz.³ Using equivalent initial concentrations (a) of oxalic acid and bromine between $M/40$ and $M/160$, and without added bromides, the process was found to follow approximately the kinetic equation :

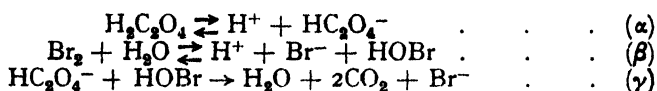
$$dx/dt = k_0(a - x)^2/x^2 \quad (I)$$

The rate of reaction was shown to be increased by the addition of sodium sulphate and to be decreased by nitric, hydrochloric, and hydrobromic acids and by bromides. In the presence of these retarding agents, Józefowicz expresses the rate by a series of empirical equations of the type :

$$dx/dt = k_0(a - x)^2/(kc + x)^2 \quad (II)$$

where c is the concentration of added substance, and k is a constant dependent on the nature of the addition. For hydrobromic acid, which has the greatest retarding influence, k is unity ; for neutral bromides k is $3/5$; and for hydrochloric and nitric acids k is $1/5$. The oxidation of acid-oxalates by bromine is also stated by Józefowicz to obey kinetic equation I, the value of k_0 , however, being now about three times as great as in the case of oxalic acid. For neutral oxalates, according to this author, the rate of reaction is too high to permit of measurement.

Józefowicz has attempted to interpret his results by the hypothesis that the measured reaction in solutions containing bromine and oxalic acid is a reaction between HC_2O_4^- ions and HOBr , the latter present in small amount as a product of hydrolysis of bromine ; thus :



His treatment of the reaction kinetics on this basis is, however, only qualitative, and entirely inadequate to establish or refute the mechanism. Indeed, he is led to the view that the above scheme fails to interpret completely the relative retarding effects of the hydrogen and bromide ions, and he consequently suggests that, in addition to reaction (γ), there may also be a direct interaction between bromine molecules and $\text{C}_2\text{O}_4^{2-}$ ions. No justification of the empirical equations I and II is given ; actually, it is easy to see that the kinetic law resulting from such a mechanism as that postulated will be much more elaborate than, and bear little formal resemblance to, these equations. Finally, the relative velocity of oxidation of acid-oxalates is not discussed in terms of the mechanism proposed.

Having regard for the obvious discrepancies between the conclusions of Józefowicz and those of Roloff and of Berthoud and Bellenot, we have carried out a number of kinetic measurements on the bromine-oxalate reaction over a very wide range of conditions, the result of which has been to substantiate the mechanism of Józefowicz as expressed by

³ Józefowicz, *Rocz. Chem.*, **8**, 123, 1928.

equations (α), (β) and (γ). The mechanism is found to be applicable to the oxidation by bromine not only of oxalic acid but also of acid oxalates, neutral oxalates, and mixtures of these; that is, it has been tested and proven for solutions covering an acidity range from $p_H = 4.5$ to $p_H = 1$. The somewhat complex differential equations representing the course of reaction under various conditions have been integrated, and velocity constants calculated for each reaction mixture. These constants, which are compounded of a real velocity constant and several equilibrium constants, vary somewhat with the ionic strength of the reaction mixture, but an analysis of the data has made possible the estimation of (i) the value of the second dissociation constant of oxalic acid and its variation with ionic strength; (ii) the effect of ionic strength on the velocity constant of the reaction: $\text{HC}_2\text{O}_4^- + \text{HOBr} \rightarrow \text{H}_2\text{O} + 2\text{CO}_2 + \text{Br}^-$ which determines the measured rate.

For the interpretation of the kinetic measurements it has been found necessary to investigate the variation of the equilibrium constant of the process $\text{Br}_2 + \text{Br}^- \rightleftharpoons \text{Br}_3^-$ with ionic strength in solutions of KBr, NaBr, and HBr. The results of this subsidiary investigation are given in the preceding paper.

Experimental.

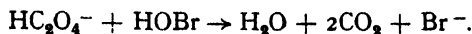
The bromine and the bromides employed were the preparations described in the preceding paper (p. 102). Various samples of oxalic acid and of sodium and potassium oxalates have been used, including Merck's and Kahlbaum's preparations and products recrystallised by us. Solutions of acid oxalate were made by mixing solutions of oxalic acid and neutral oxalate in the requisite proportions. Reaction mixtures were contained in small, well-stoppered glass bottles, painted black to exclude light, and suspended in a thermostat which was regulated to $\pm 0.03^\circ \text{C}$. The reaction was followed by pipetting out samples of the reaction mixture and estimating the bromine content by running into sodium arsenite solution (containing excess NaHCO_3) and titrating with iodine using starch as indicator. Measurements have been carried out at the three temperatures 21.5° , 16.5° , and 11.5° , and with the following reaction mixtures:

- (a) (1) $\text{Br}_2 + \text{K}_2\text{C}_2\text{O}_4 + \text{KHC}_2\text{O}_4 + \text{KBr}$.
- (2) $\text{Br}_2 + \text{Na}_2\text{C}_2\text{O}_4 + \text{NaHC}_2\text{O}_4 + \text{NaBr}$.
- (b) (1) $\text{Br}_2 + \text{KHC}_2\text{O}_4 + \text{KBr}$.
- (2) $\text{Br}_2 + \text{NaHC}_2\text{O}_4 + \text{NaBr}$.
- (c) (1) $\text{Br}_2 + \text{H}_2\text{C}_2\text{O}_4 + \text{KBr}$.
- (2) $\text{Br}_2 + \text{H}_2\text{C}_2\text{O}_4 + \text{NaBr}$.
- (3) $\text{Br}_2 + \text{H}_2\text{C}_2\text{O}_4 + \text{HBr}$.

The total ionic strength of the reaction mixture has been varied from 0.0 to 0.8, and the bromide concentration from 0.0 to 0.5 *N*. The concentrations of oxalic acid and of neutral and acid oxalates have been varied as far as their limited solubilities and the practicability of kinetic measurement permitted. Finally, the initial bromine concentration has been varied between $M/30$ and $M/600$, though most of the measurements were effected with $M/80 \text{ Br}_2$. The initial concentration of bromine was never greater than that of the oxalate.

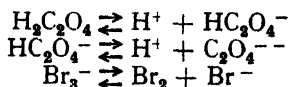
Formulation of the Reaction Kinetics.

In what follows all concentrations are expressed in moles per litre, and the initial concentrations of reactants are represented by the symbols : total titratable bromine = a , neutral oxalate = b , acid-oxalate = e , oxalic acid = d , bromide (or HBr) = c . The symbol x is used to denote the fall in total bromine concentration after a time t (in minutes) has elapsed. As already indicated, it has been found possible to interpret all our measurements in terms of a single reaction which determines the observed rate, *viz.* :

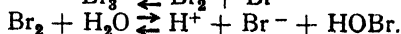


Let the velocity constant of this process be k .

To evaluate the concentrations of the reacting entities HC_2O_4^- and HOBr , we have to take into consideration the four inter-dependent equilibria :



and



These equilibria are defined by the equilibrium constants :

$$K_1 = \frac{[\text{H}^+][\text{HC}_2\text{O}_4^-]}{[\text{H}_2\text{C}_2\text{O}_4]} \quad (1) \quad K_2 = \frac{[\text{H}^+][\text{C}_2\text{O}_4^{--}]}{[\text{HC}_2\text{O}_4^-]} \quad (2)$$

$$K_3 = \frac{[\text{Br}_2][\text{Br}^-]}{[\text{Br}_3^-]} \quad (3) \quad K = \frac{[\text{H}^+][\text{Br}^-][\text{HOBr}]}{[\text{Br}_2]} \quad (4)$$

The instantaneous rate of reaction is then given by

$$-\frac{d(a-x)}{dt} = \frac{dx}{dt} = k[\text{HOBr}][\text{HC}_2\text{O}_4^-] = kK \frac{[\text{Br}_2]}{[\text{Br}^-][\text{H}^+]} [\text{HC}_2\text{O}_4^-] \quad (5)$$

To convert this into a form convenient for integration, we must express the continuously varying quantities $[\text{Br}_2]$, $[\text{Br}^-]$, $[\text{H}^+]$, and $[\text{HC}_2\text{O}_4^-]$ as functions of the known quantities, a , b , c , d , e and x .

To evaluate $[\text{Br}_2]$, we combine equation (3) with the equation :

$$\text{titratable bromine} = a - x = [\text{Br}_2] + [\text{Br}_3^-] + [\text{HOBr}] \quad (6)$$

and neglecting the $[\text{HOBr}]$ term,* obtain

$$[\text{Br}_2] = \frac{K_3}{K_3 + [\text{Br}^-]}(a - x). \quad (7)$$

$[\text{Br}^-]$ is calculated as follows. At the start of the reaction we have

$$\begin{aligned}a &= [\text{Br}_2] + [\text{Br}_3^-] + [\text{HOBr}], \\ \text{and} \quad c &= [\text{Br}^-] + [\text{Br}_3^-].\end{aligned}$$

At time t , similarly :—

$$\begin{aligned}a - x &= [\text{Br}_2] + [\text{Br}_3^-] + [\text{HOBr}], \\ \text{and} \quad c + 2x &= [\text{Br}^-] + [\text{Br}_3^-].\end{aligned}$$

* This neglect may be shown to be permissible. Under the most extreme conditions of this work, *i.e.*, low $[\text{H}^+]$ and low $[\text{Br}^-]$, not more than 1 per cent. of the titratable bromine is present as HOBr .

Combining these with equation (3) and again neglecting $[\text{HOBr}]$, we find

$$[\text{Br}^-]_0 = \frac{1}{2}\{(c - a - K_3) + \sqrt{(c - a - K_3)^2 + 4K_3c}\} \quad (8)$$

and

$$[\text{Br}^-]_t = \frac{1}{2}\{(c - a - K_3 + 3x) + \sqrt{(c - a - K_3 + 3x)^2 + 4K_3(c + 2x)}\} \quad (9)$$

From these equations it has been found that, in all our experiments, $[\text{Br}^-]$ is, to a sufficiently close approximation, a linear function of x ; that is

$$[\text{Br}^-]_t = [\text{Br}^-]_0 + z \cdot x \quad (10)$$

where z is a constant for a given experiment.

Substituting now the values of $[\text{Br}_2]$ and $[\text{Br}^-]$ from equations (7) and (10) in (5), we find

$$\frac{dx}{dt} = kK_3 \cdot \frac{a - x}{\{[\text{Br}^-]_0 + zx\}\{[\text{Br}^-]_0 + K_3 + zx\}} \cdot \frac{[\text{HC}_2\text{O}_4^-]}{[\text{H}^+]}$$

Writing now

$$\begin{aligned} & \frac{[\text{Br}^-]_0/z = \alpha_1}{\{[\text{Br}^-]_0 + K_3\}/z = \alpha_2} \end{aligned} \quad (11)$$

$$\text{then} \quad \frac{dx}{dt} = \frac{kK_3}{z^2} \cdot \frac{a - x}{(\alpha_1 + x)(\alpha_2 + x)} \cdot \frac{[\text{HC}_2\text{O}_4^-]}{[\text{H}^+]} \quad (12)$$

There remains to be expressed in terms of measurable quantities the concentrations of H^+ and HC_2O_4^- or their ratio $[\text{HC}_2\text{O}_4^-]/[\text{H}^+]$. Owing to the wide range of conditions investigated, it is necessary to treat separately the following cases: (a) solutions containing neutral oxalate and acid oxalate; (b) solutions of acid oxalate; (c) solutions of oxalic acid; and (d) solutions containing oxalic acid and a mineral acid (HBr).

(a) Solutions containing Neutral Oxalate and Acid Oxalate.

The initial concentrations of the various ions in such solutions are defined by equations (1) and (2), together with

$$[\text{H}_2\text{C}_2\text{O}_4] + [\text{HC}_2\text{O}_4^-] + [\text{C}_2\text{O}_4^{--}] = b + e$$

$$\text{and} \quad 2b + e + [\text{H}^+] = [\text{HC}_2\text{O}_4^-] + 2[\text{C}_2\text{O}_4^{--}].$$

From these we obtain for $[\text{C}_2\text{O}_4^{--}]$

$$\frac{K_2(2b + e - 2[\text{C}_2\text{O}_4^{--}])^2[\text{C}_2\text{O}_4^{--}]}{K_1([\text{C}_2\text{O}_4^{--}] - K_2)^2} + \frac{(2b + e - 2[\text{C}_2\text{O}_4^{--}])[\text{C}_2\text{O}_4^{--}]}{[\text{C}_2\text{O}_4^{--}] - K_2} = b + e \quad (13)$$

This equation may be solved for $[\text{C}_2\text{O}_4^{--}]$ by the method of trial and error. Similarly for the concentration of $\text{C}_2\text{O}_4^{--}$ after a time t , we find

$$\begin{aligned} & \frac{K_2(2b + e - 2[\text{C}_2\text{O}_4^{--}] - 2x)^2[\text{C}_2\text{O}_4^{--}]}{K_1([\text{C}_2\text{O}_4^{--}] - K_2)^2} \\ & + \frac{(2b + e - 2[\text{C}_2\text{O}_4^{--}] - 2x)[\text{C}_2\text{O}_4^{--}]}{[\text{C}_2\text{O}_4^{--}] - K_2} + [\text{C}_2\text{O}_4^{--}] = b + e - x \end{aligned} \quad (14)$$

For various values of x , the values of $[\text{C}_2\text{O}_4^{--}]$ corresponding to various extents of reaction may now be calculated from (14). From these it is found that, in each reaction mixture investigated, $[\text{C}_2\text{O}_4^{--}]$ varies linearly with x ; that is, we write

$$[\text{C}_2\text{O}_4^{--}]_t = [\text{C}_2\text{O}_4^{--}]_0 - mx \quad (15)$$

where $[C_2O_4^{--}]_0$ is, of course, the value of $[C_2O_4^{--}]$ given by equation (13), and m is a constant slightly less than unity.

It should be remarked, however, that it is necessary to derive equation (15) *via* (13) and (14) only for mixtures in which the acid oxalate is in excess of the neutral oxalate, or in which the concentration of neutral oxalate is small. In the great majority of our experiments, however, the conditions were such that it is sufficiently accurate to write

$$[C_2O_4^{--}]_0 = b \quad . \quad . \quad . \quad . \quad (16)$$

$$\text{and} \quad [C_2O_4^{--}]_t = b - x \quad . \quad . \quad . \quad . \quad (17)$$

This point is emphasised because in these experiments the value of the velocity constant $\frac{kKK_3}{K_2}$ calculated from the kinetic data (see below) is then arrived at without the necessity of ascribing specific values to K_1 and K_2 , the two ionisation constants of oxalic acid.

For the general case, combining (15) with (12), noting that

$$[HC_2O_4^-]/[H^+] = [C_2O_4^{--}]/K_2, \text{ and writing } [C_2O_4^{--}]/m = b'$$

we obtain

$$\frac{dx}{dt} = \frac{kKK_3}{K_2} \cdot \frac{m}{z^3} \cdot \frac{(a-x)(b'-x)}{(\alpha_1+x)(\alpha_2+x)} \quad . \quad . \quad . \quad (18)$$

Integration of this gives

$$\frac{kKK_3}{K_2} = \frac{z^2}{m} \cdot \frac{1}{t} \left\{ x + \frac{(a+\alpha_1)(a+\alpha_2)}{b'-a} \log_e \frac{a}{a-x} - \frac{(b'+\alpha_1)(b'+\alpha_2)}{b'-a} \log_e \frac{b'}{b'-x} \right\} \quad . \quad (19)$$

(b) Solutions of Acid Oxalate.

In equations (13) and (14) the second terms of the left-hand sides represent $[HC_2O_4^-]_0$ and $[HC_2O_4^-]_t$ respectively. For solutions of acid oxalate we obtain the same equations with b now equal to zero; from these we calculate $[HC_2O_4^-]_0$, $[HC_2O_4^-]_t$, $[C_2O_4^{--}]_0$ and $[C_2O_4^{--}]_t$. By application of equation (2) we then obtain $[H^+]_0$ and $[H^+]_t$, and therefrom the ratio $[H^+]/[HC_2O_4^-]$ initially and for various values of x . It is then possible to express this ratio as a function of x ; in this case a quadratic function of x is required of the type:

$$\frac{[H^+]}{[HC_2O_4^-]} = h_0 + Rx + Sx^2 \quad . \quad . \quad . \quad (20)$$

where h_0 is the initial value of the ratio, and R and S are constants for a given experiment. Substituting (20) in (12),

$$\frac{dx}{dt} = \frac{kKK_3}{z^3} \cdot \frac{a-x}{(\alpha_1+x)(\alpha_2+x)} \cdot \frac{1}{h_0 + Rx + Sx^2} \quad . \quad . \quad (21)$$

Integration then gives

$$\begin{aligned} kKK_3 = \frac{z^2}{t} & \left\{ (\alpha_1+a)(\alpha_2+a)(h_0+Ra+Sa^2) \log_e \frac{a}{a-x} \right. \\ & - \frac{(\alpha_1+a)(\alpha_2+a)(h_0+Ra+Sa^2) - h_0\alpha_1\alpha_2}{a} \cdot x \\ & - \frac{(\alpha_1+a)(\alpha_2+a)(h_0+Ra+Sa^2) - h_0\alpha_1\alpha_2 - a[R\alpha_1\alpha_2 + h_0(\alpha_1+\alpha_2)]}{2a^2} \cdot x^2 \\ & \left. - \frac{S(\alpha_1+\alpha_2+a)+R}{3} \cdot x^3 - \frac{S}{4} \cdot x^4 \right\} \quad . \quad . \quad . \quad (22) \end{aligned}$$

(c) *Solutions of Oxalic Acid.*

In this case, $[H^+]$ is sufficiently great to permit us to neglect the dissociation of $HC_2O_4^-$. We may therefore write :

$$\Delta = [H^+]_0 = [HC_2O_4^-]_0 = \frac{1}{2}\{\sqrt{K_1^2 + 4dK_1} - K_1\} \quad (23)$$

After a time t ,

$$[H^+] = [HC_2O_4^-] + 2x \text{ and } [H_2C_2O_4] + [HC_2O_4^-] = d - x.$$

Hence from equation (1)

$$[HC_2O_4^-]_t = \frac{1}{2}\{\sqrt{K_1^2 + 4dK_1 + 4x^2} - (K_1 + 2x)\} \quad (24)$$

and

$$[H^+]_t = \frac{1}{2}\{\sqrt{K_1^2 + 4dK_1 + 4x^2} - (K_1 - 2x)\} \quad (25)$$

It is sufficiently accurate to neglect the $4x^2$ terms in these, and thus

$$\left. \begin{aligned} [HC_2O_4^-]_t &= \Delta - x \\ [H^+]_t &= \Delta + x \end{aligned} \right\} \quad (26)$$

Substituting in (12), we obtain

$$\frac{dx}{dt} = \frac{kKK_3}{x^2} \cdot \frac{a-x}{(\alpha_1+x)(\alpha_2+x)} \cdot \frac{\Delta-x}{\Delta+x} \quad (27)$$

Integration gives

$$\begin{aligned} kKK_3 = \frac{x^2}{t} & \left\{ \frac{1}{2}x^2 + (\alpha_1 + \alpha_2 + a + 2\Delta)x \right. \\ & \left. + \frac{(a+\Delta)(a+\alpha_1)(a+\alpha_2)}{\Delta-a} \log_e \frac{a}{a-x} - \frac{2\Delta(\Delta+\alpha_1)(\Delta+\alpha_2)}{\Delta-a} \log_e \frac{\Delta}{\Delta-x} \right\} \end{aligned} \quad (28)$$

(d) *Solutions of Oxalic Acid and HBr.*

In this case, assuming the HBr completely ionised, we obtain

$$\begin{aligned} [HC_2O_4^-]_t &= \frac{1}{2}\{\sqrt{K_1^2 + 4dK_1 + c^2 + 4x^2 + 2K_1c + 4cx} - (K_1 + c + 2x)\} \\ [H^+]_t &= \frac{1}{2}\{\sqrt{K_1^2 + 4dK_1 + c^2 + 4x^2 + 2K_1c + 4cx} - (K_1 - c - 2x)\}. \end{aligned}$$

Calculating $[HC_2O_4^-]$ and $[H^+]$ for various values of x , we find they can be expressed sufficiently accurately as linear functions of x , viz.

$$\begin{aligned} [H^+]_t &= \Delta_1 + u \cdot x \\ [HC_2O_4^-]_t &= \Delta_2 - v \cdot x. \end{aligned}$$

Substituting these in equation (12), placing $\frac{\Delta_1}{u} = \Delta_1'$ and $\frac{\Delta_2}{v} = \Delta_2'$ and integrating, we find

$$\begin{aligned} kKK_3 = \frac{uvx^3}{vt} & \left\{ \frac{1}{2}x^3 + (\alpha_1 + \alpha_2 + a + \Delta_1' + \Delta_2')x \right. \\ & + \frac{(a+\Delta_1')(a+\alpha_1)(a+\alpha_2)}{\Delta_2'-a} \log_e \frac{a}{a-x} \\ & \left. - \frac{(\Delta_2' + \Delta_1')(\Delta_2' + \alpha_1)(\Delta_2' + \alpha_2)}{\Delta_2'-a} \log_e \frac{\Delta_2'}{\Delta_2'-x} \right\} \quad (29) \end{aligned}$$

Equations (19), (22), (28) and (29) are the ones used for the analysis of our kinetic data. It is to be noted that in case (a) namely solutions containing neutral oxalate and acid oxalate, the constant calculated is

kKK_3/K_2 while in all other cases it is kKK_3 . By dividing one set of constants by the other we thus have a method, based entirely on kinetic measurements, of determining K_2 , the second dissociation constant of oxalic acid. It might be objected that in calculating these velocity constants a pre-knowledge of the values of K_1 , K_2 and K_3 is necessary, and that consequently the values of K_2 finally obtained are not really independent values. That this objection is not valid, however, is easily demonstrated. The computation of kKK_3 in cases (c) and (d) involves no assumption regarding K_2 , and the same applies to the values of kKK_3/K_2 calculated from the great majority of experiments in case (a), *viz.*, in those experiments for which equation (16) and (17) hold. From these cases, then, the values of K_2 are independently derived. It is these values of K_2 which are used in the calculation of kKK_3 for case (b). and it is significant that the figures for kKK_3 thus obtained are in reasonable accord with the others.

Values of the Constants K_1 , K_2 and K_3 .

The value of K_3 , the equilibrium constant of tribromide formation,

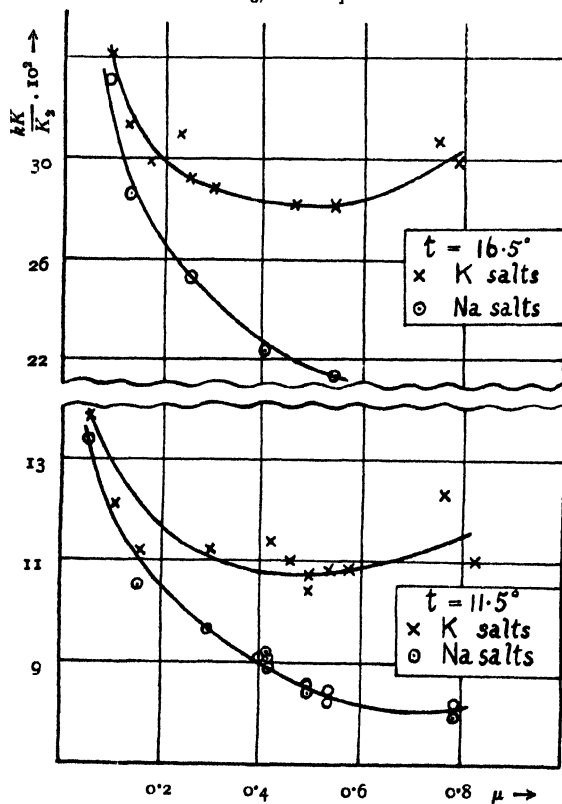


FIG. 1.

$$\log_{10} K_1 = 2.756 + 0.42\sqrt{\mu} - 0.275\mu;$$

$$\log_{10} K_2 = 5.857 + 0.81\sqrt{\mu} - 0.39\mu.$$

⁴ Dawson, *J.C.S.*, pp. 1884, 2530, 1929; p. 79, 1930.

is required in the calculation of each experiment. It was shown in the preceding paper that K_3 varies with temperature, with ionic strength, and with the cation present. We have used values of K_3 at 21.5° and 16.5° given by the curves of Fig. 1, p. 104, and have derived the values required at 11.5° from the temperature coefficient of K_3 .

As regards K_1 and K_2 , the first and second dissociation constants of oxalic acid, these are stated by Dawson and his co-workers⁴ to vary considerably with the ionic strength of the solution. In presence of potassium chloride of ionic strength μ , they find

In the absence of other data we have used the values of K_1 given by the first of these equations in our kinetic calculations. The propriety of this is discussed later (p. 122). It may here be remarked, however, that any error in the value of K_1 used involves a much less than proportionate error in the calculated constants kKK_3/K_2 and kKK_3 of cases (a) and (c). On the other hand, the constant kKK_3 of cases (b) and (d) is more sensitive to the value of K_1 used in the calculation.

The values of K_2 which we have employed throughout are not those of Dawson, but those derived from our own kinetic measurements, *viz.*, from the constants kKK_3/K_2 and kKK_3 of cases (a) and (c) respectively. Discussion of these K_2 values is best deferred till after the presentation of the kinetic data themselves.

Summary of Kinetic Data.

To illustrate the mode of calculation of the velocity constants, we reproduce the details of a typical experiment.

TABLE I.

Reaction mixture :

$M/40K_2C_2O_4 + M/40KHC_2O_4 + M/16KBr + M/80$ (approx.) Br_2
Temp. = $11.5^\circ C.$; $a = 0.01185$; $b = c = 0.025$; $c = 0.0625$; $\mu = 0.16$;

$$K_1 = 7.6 \times 10^{-2}; K_2 = 1.7 \times 10^{-5}; K_3 = 5.31 \times 10^{-2}.$$

From (13), (14) and (15), $[C_2O_4^{--}]_t = 0.02516 - 0.99x$

$$\text{and} \quad b' = \frac{0.02516}{0.99} = 0.02542.$$

From (8) and (9),

$$[Br^-]_0 = 0.056375; [Br^-]_{x=0.004} = 0.06629; [Br^-]_{x=0.008} = 0.07621;$$

whence $[Br^-]_t = [Br^-]_0 + x = 0.056375 + 2.48x$.

$$\text{From (11),} \quad \alpha_1 = 0.02274 \text{ and } \alpha_2 = 0.04416.$$

Now, in equation (19),

$$\frac{(a + \alpha_1)(a + \alpha_2)}{b' - a} \times 2.303 = \text{antilog. } \bar{I}.5170 = P,$$

$$\text{and} \quad \frac{(b' + \alpha_1)(b' + \alpha_2)}{b' - a} \times 2.303 = \text{antilog. } \bar{I}.7649 = Q.$$

$t.$	$a - x.$	$x.$	$P \log_{10} \frac{a}{a - x}$	$Q \log_{10} \frac{b'}{b' - x}$	$\frac{kKK_3}{K_2}$	$\frac{kK}{K_2}$
0.00	0.01185	—	—	—	—	—
9.47	0.009594	0.002256	0.03016	0.02349	0.005894	—
17.00	0.008294	0.003556	0.05094	0.03807	0.005999	—
28.88	0.006898	0.004952	0.07729	0.05478	0.005880	Mean
44.68	0.005534	0.006316	0.1087	0.07219	0.005951	=
60.52	0.004577	0.007273	0.1359	0.08519	0.005948	0.1116
88.03	0.003409	0.008441	0.1779	0.1020	0.005948	—
128.15	0.002361	0.009489	0.2304	0.1181	0.005898	—

116 THE KINETICS OF THE BROMINE-OXALATE REACTION

In Tables II.-VII. are summarised the results of about eighty kinetic experiments, grouped for convenience according to the temperature and the type of reaction mixture concerned. The various columns of the Tables indicate the initial stoichiometric composition of the reaction mixture with respect to oxalate, acid oxalate, oxalic acid, bromide, and bromine, its total ionic strength (as defined by Lewis and Randall, *Thermodynamics*), and the pertinent velocity constant kK/K_2 or kK calculated from equation (19), (22), (28) or (29). Each velocity constant is, of course, the mean of the five to eight separate values obtained in each experiment.

TABLE II.—MIXTURES CONTAINING $K_2C_2O_4$, KHC_2O_4 AND KBr .

Initial Concentrations.				Ionic Strength μ .	$\frac{Kk}{K_1} \cdot 10^3$.
$K_2C_2O_4$.	KHC_2O_4 .	KBr.	Br_2 .		

Temperature = 11.5°.

<i>M/6</i>	<i>M/12</i>	<i>M/4</i>	<i>M/80</i>	0.833	10.96
<i>M/12</i>	<i>M/48</i>	<i>M/2</i>	<i>M/80</i>	0.771	12.28
<i>M/12</i>	<i>M/12</i>	<i>M/4</i>	<i>M/80</i>	0.583	10.80
<i>M/12</i>	<i>M/24</i>	<i>M/4</i>	<i>M/80</i>	0.542	10.84
<i>M/12</i>	<i>M/24</i>	<i>5M/24</i>	<i>M/80</i>	0.500	10.71
<i>M/16</i>	<i>M/16</i>	<i>M/4</i>	<i>M/80</i>	0.500	10.38
<i>M/24</i>	<i>M/12</i>	<i>M/4</i>	<i>M/80</i>	0.458	10.98
<i>M/12</i>	<i>M/24</i>	<i>M/8</i>	<i>M/30</i>	0.420	11.36
<i>M/20</i>	<i>M/40</i>	<i>M/8</i>	<i>M/80</i>	0.300	11.21
<i>M/40</i>	<i>M/40</i>	<i>M/16</i>	<i>M/80</i>	0.160	11.02
<i>M/40</i>	<i>M/40</i>	<i>M/16</i>	<i>M/80</i>	0.160	11.16
<i>M/80</i>	<i>M/80</i>	<i>M/16</i>	<i>M/80</i>	0.112	12.12
<i>M/160</i>	<i>M/160</i>	<i>M/32</i>	<i>M/200</i>	0.056	13.82

Temperature = 16.5°.

<i>M/12</i>	<i>M/24</i>	<i>M/2</i>	<i>M/80</i>	0.79	29.7
<i>M/12</i>	<i>M/4</i>	<i>M/4</i>	<i>M/80</i>	0.75	30.5
<i>M/12</i>	<i>M/24</i>	<i>M/4</i>	<i>M/80</i>	0.54	27.9
<i>M/24</i>	<i>M/12</i>	<i>M/4</i>	<i>M/80</i>	0.46	27.9
<i>M/30</i>	<i>M/30</i>	<i>M/6</i>	<i>M/30</i>	0.30	28.7
<i>M/40</i>	<i>M/40</i>	<i>6M/40</i>	<i>M/80</i>	0.25	29.0
<i>M/40</i>	<i>M/320</i>	<i>6M/40</i>	<i>M/100</i>	0.23	30.8
<i>M/80</i>	<i>M/20</i>	<i>M/12</i>	<i>M/100</i>	0.17	29.7
<i>M/80</i>	<i>M/80</i>	<i>M/12</i>	<i>M/80</i>	0.13	31.1
<i>M/160</i>	<i>M/160</i>	<i>M/16</i>	<i>M/200</i>	0.087	34.0

Temperature = 21.5°.

<i>M/24</i>	<i>M/12</i>	<i>M/4</i>	<i>M/80</i>	0.46	71.0
<i>M/48</i>	<i>5M/48</i>	<i>M/8</i>	<i>M/200</i>	0.30	75.3

TABLE III.—MIXTURES CONTAINING $\text{Na}_2\text{C}_2\text{O}_4$, NaHC_2O_4 and NaBr .

Initial Concentrations.				Ionic Strength μ .	$\frac{kK}{K_1} \cdot 10^3$.
$\text{Na}_2\text{C}_2\text{O}_4$.	NaHC_2O_4 .	NaBr .	Br_2 .		

<i>Temperature = 11.5°.</i>					
$M/12$	$M/24$	$M/2$	$M/80$	0.79	8.20
$M/12$	$M/24$	$M/2$	$M/30$	0.79	7.93
$M/12$	$M/24$	$M/4$	$M/80$	0.54	8.44
$M/12$	$M/24$	$M/4$	$M/80$	0.54	8.22
$M/12$	$M/24$	$5M/24$	$M/80$	0.50	8.57
$M/16$	$M/16$	$M/4$	$M/80$	0.50	8.43
$M/12$	$M/24$	$M/8$	$M/80$	0.42	9.10
$M/12$	$M/24$	$M/8$	$M/80$	0.42	8.88
$M/12$	$M/24$	$M/8$	$M/30$	0.42	9.22
$M/32$	$M/16$	$M/4$	$M/80$	0.40	9.08
$M/20$	$M/40$	$M/8$	$M/80$	0.30	9.63
$M/40$	$M/40$	$M/16$	$M/80$	0.16	10.52
$M/160$	$M/160$	$M/32$	$M/200$	0.056	13.40

<i>Temperature = 16.5°.</i>					
$M/12$	$M/24$	$M/4$	$M/80$	0.54	21.2
$M/32$	$M/16$	$M/4$	$M/80$	0.40	22.2
$M/40$	$M/40$	$6M/40$	$M/80$	0.25	25.1
$M/80$	$M/80$	$M/12$	$M/80$	0.13	28.4
$M/160$	$M/160$	$M/16$	$M/200$	0.087	33.0

The results of Tables II. and III. are shown graphed in Fig. 1 (p. 114), in which the velocity constant kK/K_2 is plotted against the ionic strength μ .

TABLE IV.—MIXTURES CONTAINING OXALIC ACID AND KBr.

Initial Concentrations			Ionic Strength *	$kK \cdot 10^4$.
$\text{H}_2\text{C}_2\text{O}_4$.	KBr.	Br_2 .		
<i>Temperature = 11.5°.</i>				
$M/8$	$M/64$	$M/80$	0.081	1.96
$M/8$	$M/120$	$M/80$	0.073	1.78
$M/16$	$M/120$	$M/80$	0.048	1.83
$M/64$	$M/250$	$M/80$	0.017	1.62
$M/16$	—	$M/80$	0.04	1.65
<i>Temperature = 16.5°.</i>				
$M/16$	$M/8$	$M/120$	0.166	5.49
$M/8$	$M/32$	$M/80$	0.096	5.01
$M/8$	$M/64$	$M/80$	0.081	4.79
$M/8$	$M/120$	$M/80$	0.073	4.52
$M/64$	$M/64$	$M/120$	0.028	4.21
<i>Temperature = 21.5°.</i>				
$M/16$	$M/2$	$M/80$	0.541	17.2
$M/16$	$M/4$	$M/80$	0.291	15.0
$M/16$	$M/8$	$M/80$	0.166	13.1
$M/8$	$M/16$	$M/80$	0.129	12.5
$M/8$	$M/32$	$M/80$	0.097	12.15
$M/8$	$M/64$	$M/80$	0.081	11.7
$M/16$	$M/32$	$M/80$	0.071	11.4
$M/64$	$M/64$	$M/160$	0.028	9.73
$M/200$	$M/200$	$M/600$	0.0096	8.86

118 THE KINETICS OF THE BROMINE-OXALATE REACTION

TABLE V.—MIXTURES CONTAINING OXALIC ACID AND NaBr.

Initial Concentrations			Ionic Strength * μ	$kK \cdot 10^3$
$H_2C_2O_4$	NaBr.	Br_2		
<i>Temperature = 16.5°.</i>				
$M/16$	$M/8$	$M/120$	0.166	5.30
<i>Temperature = 21.5°.</i>				
$M/16$	$M/2$	$M/80$	0.541	14.35
$M/16$	$M/4$	$M/80$	0.291	13.05
$M/16$	$M/8$	$M/80$	0.166	12.20
$M/16$	$M/32$	$M/80$	0.071	11.00
$M/64$	$M/64$	$M/160$	0.028	9.69
$M/200$	$M/200$	$M/600$	0.0096	8.84

TABLE VI.—MIXTURES CONTAINING OXALIC ACID AND HBr.

Initial Concentrations			Ionic Strength \uparrow μ	$kK \cdot 10^3$
$H_2C_2O_4$	HBr.	Br_2		

Temperature = 21.5°.

2M/5	M/32	M/80	0.16	12.25
M/16	M/32	M/80	0.066	12.06
M/16	M/32	M/80	0.066	11.64
M/32	M/64	M/80	0.036	9.72
M/64	M/64	M/120	0.027	10.3

TABLE VII.—MIXTURES CONTAINING KHC_2O_4 AND KBr.

Initial Concentrations.			Ionic Strength μ .	$kK \cdot 10^5$.
KHC_2O_4 .	KBr.	Br_2 .		
<i>Temperature = 11.5°.</i>				
$M/8$	$M/16$	$M/80$	0.19	2.00
<i>Temperature = 16.5°.</i>				
$M/5$	$M/4$	$M/80$	0.45	6.19
$M/8$	$M/8$	$M/80$	0.25	5.39
$M/8$	$M/16$	$M/80$	0.19	5.08
<i>Temperature = 21.5°.</i>				
$M/4$	$M/4$	$M/80$	0.50	15.0
$M/8$	$M/8$	$M/80$	0.25	13.1
$M/32$	$M/12$	$M/80$	0.11	11.8

* The ionic strength of these solutions is defined as the stoichiometric concentration of bromide *plus* the concentration of H^+ (the Δ of the equation (23)).

† The ionic strength of these solutions is the concentration of H^+ .

The results of Tables IV., V., and VII. are shown graphically in Fig. 2, in which the velocity constant kK is plotted against μ .

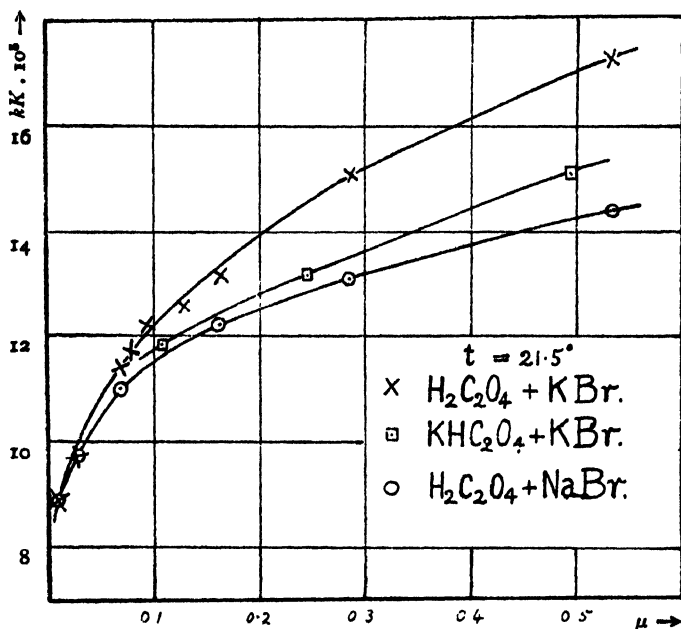


FIG. 2.

Discussion of Results.

The results presented above, corresponding as they do to a very wide range of experimental conditions, must be regarded as a fairly satisfactory confirmation of the postulated mechanism. Although, as will be seen from Figs. 1 and 2, the values of kK/K_2 and kK are to some extent dependent on the ionic strength of the reacting system, these variations are, as we shall show, largely explicable in terms of the dependence of the separate constants k , K and K_2 upon μ .

There are two characteristics of the mechanism, which assumes $\text{HC}_2\text{O}_4^- + \text{HOBr} \rightarrow \text{H}_2\text{O} + 2\text{CO}_2 + \text{Br}^-$ as the rate-determining process, to which attention is directed. It postulates (a) that, independent of the hydrogen ion content, the rate should be proportional to the ratio $[\text{HC}_2\text{O}_4^-]/[\text{H}^+]$, and (b) that the effect of bromide is expressed by rate being

proportional to the function $\frac{1}{[\text{Br}^-]\{K_3 + [\text{Br}^-]\}}$. The Roloff mechanism, in which the rate-determining process is assumed to be a reaction between free bromine and oxalate ion, *viz.*, $\text{Br}_2 + \text{C}_2\text{O}_4^{2-} \rightarrow 2\text{Br}^- + 2\text{CO}_2$, and which also predicts (a), requires that the rate should depend on the bromide ion concentration proportionately only to $\frac{1}{[K_3 + \text{Br}^-]}$. It

follows that when the bromide ion concentration is changed from say $M/2$ to $M/32$ (cf. Table V.), the absolute rate of reaction should, *cet. par.*, increase 115 fold with the $\text{HC}_2\text{O}_4^- - \text{HOBr}$ mechanism, but only 6.5 times with the Roloff mechanism. The approximate constancy of our kK in this range is sufficient to give a clear cut decision in favour of the

mechanism we have adopted. Various comparisons of the same type in all the other Tables lead to the same result; in every case the effect of changing $[\text{Br}^-]$ is much greater than that which the Roloff mechanism forecasts. So far as we are aware, the reaction between bromine and oxalic acid (or oxalates) is the only example of an oxidation by bromine in which the reacting entity is HOBr and not the bromine molecule itself.

Temperature Coefficients of the Reaction.—Table VIII. gives values of the temperature coefficient of kK obtained from corresponding experiments with oxalic acid at two temperatures, and Table IX. similarly those of kK/K_2 from experiments with oxalates.

TABLE VIII.—TEMPERATURE COEFFICIENTS OF kK .

Reaction Mixture.	$\frac{kK \text{ at } 16.5^\circ}{kK \text{ at } 11.5^\circ}$	Mean Temperature Coefficient.
$M/8 \text{ H}_2\text{C}_2\text{O}_4 + M/64 \text{ KBr} + M/80 \text{ Br}_2$ $M/8 \text{ H}_2\text{C}_2\text{O}_4 + M/120 \text{ KBr} + M/80 \text{ Br}_2$	2.44 2.54	Mean coefficient for 5° rise = 2.44, corresponding to a temperature coefficient for 10° of 5.95.
	$\frac{kK \text{ at } 21.5^\circ}{kK \text{ at } 16.5^\circ}$	
$M/16 \text{ H}_2\text{C}_2\text{O}_4 + M/8 \text{ KBr} + M/120 \text{ Br}_2$	2.39	
$M/8 \text{ H}_2\text{C}_2\text{O}_4 + M/32 \text{ KBr} + M/80 \text{ Br}_2$	2.43	
$M/8 \text{ H}_2\text{C}_2\text{O}_4 + M/64 \text{ KBr} + M/80 \text{ Br}_2$ $M/64 \text{ H}_2\text{C}_2\text{O}_4 + M/64 \text{ KBr} + M/120 \text{ Br}_2$	2.44 2.48	

TABLE IX.—TEMPERATURE COEFFICIENTS OF kK/K_2 .

Reaction Mixture.	$\frac{kKK_2 \text{ at } 16.5^\circ}{kKK_2 \text{ at } 11.5^\circ}$	Mean Temperature Coefficient.
$M/12 \text{ K}_2\text{C}_2\text{O}_4 + M/24 \text{ KHC}_2\text{O}_4$ $+ M/4 \text{ KBr} + M/80 \text{ Br}_2$	2.57	Mean coefficient for 5° rise = 2.54, corresponding to a temperature coefficient for 10° of 6.45.
$M/32 \text{ Na}_2\text{C}_2\text{O}_4 + M/16 \text{ NaHC}_2\text{O}_4$ $+ M/4 \text{ NaBr} + M/80 \text{ Br}_2$	2.45	
$M/24 \text{ K}_2\text{C}_2\text{O}_4 + M/12 \text{ KHC}_2\text{O}_4$ $+ M/4 \text{ KBr} + M/80 \text{ Br}_2$	2.54	
	$\frac{kKK_2 \text{ at } 21.5^\circ}{kKK_2 \text{ at } 16.5^\circ}$	
$M/24 \text{ K}_2\text{C}_2\text{O}_4 + M/12 \text{ KHC}_2\text{O}_4$ $+ M/4 \text{ KBr} + M/80 \text{ Br}_2$	2.56	

Variation of K_2 with μ .—From a comparison of the curves (Figs. 1 and 2) giving the variation of kK and kK/K_2 with μ , it is possible to obtain the variation of K_2 , the second ionisation constant of oxalic acid, with ionic strength. Since, however, we have values of kK over a sufficient range of μ only at 21.5° , and values of kK/K_2 over approximately the same range of μ only at 11.5° and 16.5° , the comparison of the two sets of data has been made by first converting the values of kK/K_2 to the

temperature 21.5° , using for this purpose the temperature coefficient 6.45 (see above) which applies to these data. On this basis the derived values of K_2 are all values referring to the one temperature 21.5° . The curves compared are :—

- (1) kK at 21.5° with kK/K_2 at 16.5° } potassium salts ;
 (2) kK at 21.5° with kK/K_2 at 11.5° }
 (3) kK at 21.5° with kK/K_2 at 16.5° } sodium salts.
 (4) kK at 21.5° with kK/K_2 at 11.5° }

Table X. gives the results obtained.

TABLE X.

μ	0.05	0.1	0.2	0.3	0.4	0.5
$K_2 \cdot 10^4$ { (1) (2) (3) (4)	— 1.23 — 1.23	1.45 — 1.48 1.54	1.83 — 1.86 1.90	2.07 2.10 2.16 2.12	2.27 2.32 2.43 2.36	2.41 2.46 2.61 2.59
$K_2 \cdot 10^4$ for K salts .	1.23	1.45	1.83	2.08	2.29	2.43
$K_2 \cdot 10^4$ for Na salts .	1.23	1.51	1.88	2.14	2.40	2.60

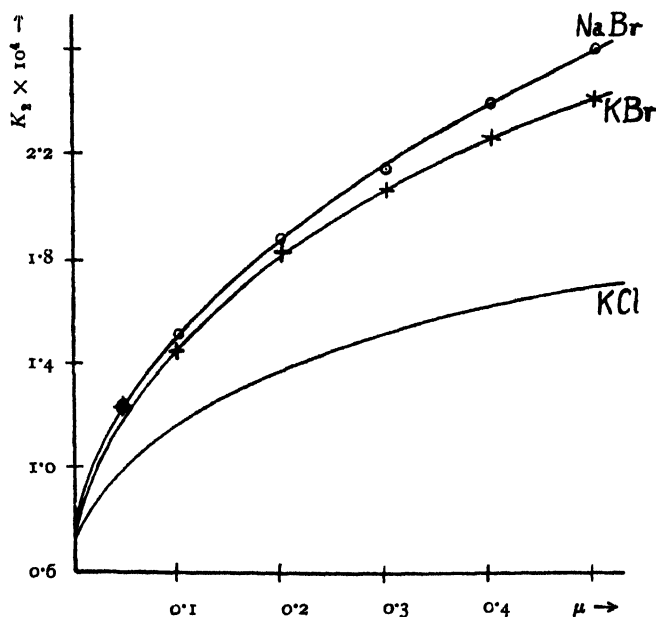


FIG. 3.

The averaged values of K_2 in presence of potassium and sodium salts are plotted against ionic strength in Fig. 3. The third plot in this figure is that of the results obtained by Dawson⁴ also from kinetic measurements, for the effect of potassium chloride on K_2 .

It will be observed that K_2 increases markedly with the ionic strength

of the solution, that the effect of sodium salts on K_2 is slightly greater than that of potassium salts, and that in both cases the neutral salt effect is definitely greater than that obtained by Dawson for potassium chloride. However, the value of K_2 at $\mu = 0$, viz., $7 \cdot 10^{-5}$, agrees remarkably well with the value $7 \cdot 2 \cdot 10^{-5}$ given by Dawson, and also is in good accord with Drucker's value⁵ of $6 \cdot 7 \cdot 10^{-5}$ obtained from conductivity, freezing-point, and *E.M.F.* data. This agreement means, of course, that over the range of $[H^+]$ in which the reaction between bromine and oxalates (oxalic acid) has here been studied, viz., $3 \cdot 10^{-5}$ to 10^{-1} , the velocity is, as the mechanism demands, proportional to the quotient $[HC_2O_4^-]/[H^+]$.

Reverting to the variation of K_2 with μ , our results are well reproduced by the empirical equations:—

In presence of K salts, $\log_{10} K_2 = \bar{5} \cdot 853 + 1 \cdot 21\sqrt{\mu} - 0 \cdot 65\mu$.

In presence of Na salts, $\log_{10} K_2 = \bar{5} \cdot 847 + 1 \cdot 21\sqrt{\mu} - 0 \cdot 58\mu$.

Dawson's equation for K_2 (in KCl solutions) is

$$\log_{10} K_2 = \bar{5} \cdot 857 + 0 \cdot 81\sqrt{\mu} - 0 \cdot 39\mu.$$

With regard to the dependence of our K_2 upon μ , it should be borne in mind that the salt effect as found by us is not a single salt effect, but is composite of the effects of bromide, oxalate, and acid oxalate always present together in the reaction mixture. Each salt effect is probably specific, however, and accordingly we cannot claim that our curves of Fig. 3 give more than a qualitative representation of the variation of K_2 with increasing concentrations of NaBr and KBr.

The values of K_2 given in Table X. and Fig. 3 are those used in the calculation of the constant kK from the kinetic data relating to acid oxalate solutions, for which calculation a rather accurate knowledge of both K_1 and K_2 is necessary. The values of K_1 used are those given by Dawson. It will be seen from Fig. 2 that the resulting values of kK are definitely lower than those obtained with oxalic acid solutions. The latter values, however, are undoubtedly the correct ones, since the value of K_2 does not enter and that of K_1 enters only to a subsidiary degree into their calculation from the experimental data. On the other hand, a recalculation of the acid oxalate data using Dawson's values for both K_1 and K_2 makes the disparity between the acid oxalate and the oxalic acid results still greater. To obtain agreement, it is necessary, using our own values of K_2 , to employ at the same time values of K_1 which are greater than those of Dawson approximately in the ratio of our own and Dawson's K_2 values. For example, at $21 \cdot 5^\circ$ and $\mu = 0 \cdot 5$, in order to bring the value of kK obtained with potassium acid oxalate and potassium bromide up to the value obtained with oxalic acid and potassium bromide (*cf.* Fig. 2), it is necessary to use $K_1 = 1 \cdot 2 \cdot 10^{-1}$ instead of Dawson's value $0 \cdot 82 \cdot 10^{-1}$ actually employed.

Finally, it is possible to obtain from our results a value for the temperature coefficient of K_2 . The temperature coefficient of kK is $5 \cdot 95$, that of kK/K_2 is $6 \cdot 45$; hence the temperature coefficient of K_2 is $0 \cdot 92$. This corresponds to a positive heat of ionisation of $HC_2O_4^-$ of $1 \cdot 3$ kilocal., a value which, however, cannot be very accurate, since it is obtained from the ratio of two large and not very different temperature coefficients.

⁵ Drucker, *Z. physikal. Chem.*, **96**, 381, 1920.

Variation of the Constants k and K with Ionic Strength and Temperature.

The results obtained from experiments with oxalic acid (Tables IV. and V. and Fig. 2) show that the product kK of these constants increases rapidly with ionic strength, and further possesses a temperature coefficient much above the normal value for a velocity constant. It is possible to give a satisfactory explanation of these facts, and also to apportion—at least approximately—the contribution of the separate constants to the variation of the product (kK) with ionic strength and with temperature.

The constant K , the hydrolytic constant of bromine, is given by

$$K = \frac{[\text{HOBr}][\text{H}^+][\text{Br}^-]}{[\text{Br}_2]}$$

The true hydrolytic constant in terms of activities (K_a) is, however,

$$K_a = \frac{a_{\text{HOBr}} \cdot a_{\text{H}^+} \cdot a_{\text{Br}^-}}{a_{\text{Br}_2}} = K \cdot \frac{\gamma_{\text{HOBr}} \cdot \gamma_{\text{H}^+} \cdot \gamma_{\text{Br}^-}}{\gamma_{\text{Br}_2}}$$

where a = activity and γ = activity coefficient.⁶ Since by definition K_a is a constant, the variation of K with ionic strength of the medium is in inverse ratio to the variation of the function $\frac{\gamma_{\text{HOBr}} \cdot \gamma_{\text{H}^+} \cdot \gamma_{\text{Br}^-}}{\gamma_{\text{Br}_2}}$.

Now experiment shows that in general on increasing the ionic strength of a solution from zero the activity coefficients of ions decrease rapidly while the activity coefficients of non-electrolytes increase though considerably less rapidly. As an approximation we may therefore assume that the change in γ_{HOBr} with increasing μ is the same as that of γ_{Br_2} , since these variations are in the same direction and not large compared with the change in the product $\gamma_{\text{H}^+} \cdot \gamma_{\text{Br}^-}$. We therefore write

$$K_a = K \cdot \gamma_{\text{H}^+} \cdot \gamma_{\text{Br}^-} \quad . \quad . \quad . \quad . \quad (30)$$

The value of K_a at 21.5° may be derived from the value 5.7×10^{-10} at 0° of Jones and Hartmann⁷ and the value 5.2×10^{-9} at 25° of Bray and Connolly,⁸ both of these figures referring to solutions of bromine in water, for which the ionic strength is practically zero. These give $K_a = 3.9 \times 10^{-9}$ at 21.5°.

The variation with ionic strength of the product $\gamma_{\text{H}^+} \cdot \gamma_{\text{Br}^-}$ in aqueous solutions of HBr in presence of KBr and of NaBr has been obtained by Harned and James⁹ from measurements of the *E.M.F.*'s of cells of the type

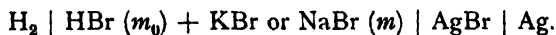


Table XI. reproduces some of their data at 25° for $[\text{HBr}] = m_0 = 0.01$ over the range of ionic strength in which we are interested. It may be mentioned that with $m = 0.1$ Harned and James found practically the same variation of $\gamma_{\text{H}^+} \cdot \gamma_{\text{Br}^-}$ with μ in presence of KBr and NaBr, and also that the corresponding data of Livingston¹⁰ for solutions of HBr

⁶ We have omitted the activity of water from the equation for K_a , since it varies by only 2 per cent. in the range from zero ionic strength to $\mu = 0.5$.

⁷ Jones and Hartmann, *Trans. Amer. Electrochem. Soc.*, **30**, 295, 1916.

⁸ Bray and Connolly, *J. Amer. Chem. Soc.*, **33**, 1485, 1911.

⁹ Harned and James, *J. Physical Chem.*, **30**, 1060, 1926.

¹⁰ Livingston, *J. Amer. Chem. Soc.*, **48**, 45, 1926.

in the absence of neutral salt are not very different. We use Harned's values in preference to those of Livingston since the conditions of the former's determinations are considered to be the closer approximation to the conditions in our experiments.

TABLE XI.—EFFECT OF BROMIDES ON THE PRODUCT $\gamma_{\text{H}^+} \cdot \gamma_{\text{Br}^-}$.

(HARNED AND JAMES.)

Temp. = 25°; [HBr] = $m_0 = 0.01$.

Total Ionic Strength $\mu = m_0 + m$	$\gamma_{\text{H}^+} \cdot \gamma_{\text{Br}^-}$	
	KBr.	NaBr.
0.01	0.835	0.835
0.05	0.706	0.709
0.11	0.638	0.643
0.21	0.593	0.608
0.31	0.564	0.590
0.51	0.554	0.594

Combining these data with $K_a = 3.9 \times 10^{-9}$, the value of K for any value of μ is obtained from equation (30). Such values of K may be combined with our experimentally determined values of the product kK to obtain the variation of the velocity constant k of the reaction $\text{HOBr} + \text{HC}_2\text{O}_4^- \rightarrow 2\text{CO}_2 + \text{H}_2\text{O} + \text{Br}^-$ with ionic strength. The results are shown in Table XII. and Fig. 4. The values of the product kK refer to 21.5° and have been read off the curves of Fig. 2.

TABLE XII.—VARIATIONS OF K and k WITH μ AT 21.5°.

μ	In Presence of KBr			In Presence of NaBr		
	$kK \times 10^5$	$K \times 10^9$	$k \times 10^{-4}$	$kK \times 10^5$	$K \times 10^9$	$k \times 10^{-4}$
0.00	(7.37)	3.9	(1.89)	(7.37)	3.9	(1.89)
0.01	8.88	4.67	1.90	8.86	4.65	1.90
0.05	10.75	5.525	1.945	10.45	5.50	1.90
0.1	12.1	6.01	2.01	11.45	5.96	1.92
0.2	13.75	6.53	2.11	12.4	6.38	1.945
0.3	15.1	6.88	2.195	13.1	6.59	1.99
0.5	16.95	7.04	2.41	14.2	6.57	2.16

From Table XII. it is seen that the bulk of the increase in kK with increasing μ —it is doubled by changing μ from 0.0 to 0.5—is due to an increase in K , the hydrolytic constant of bromine. The remainder is a small positive salt effect on the velocity constant k . This effect is greater for KBr than for NaBr, and Fig. 4 shows that for the former salt k increases linearly with μ . Further, it is seen that the bimolecular velocity constant k has a magnitude of the order $2 \cdot 10^4$, the units being

litres
moles-minutes, a very high value for such a constant. Its measurement by ordinary kinetic methods is of course rendered possible only because of the very small concentration of the reactant HOBr.

From the two direct measurements of K at 0° and 25° of Jones and Hartmann and of Bray and Connolly, it is found that K has a temperature coefficient of 2.42. Combining this with the experimentally observed temperature coefficient 5.95 of the product kK , it follows that the temperature coefficient of k itself between 11.5° and 21.5° is 2.52, corresponding to a critical increment of 15,400 calories. Thus the abnormally large increase with temperature of the observed rate of reaction between bromine and oxalic acid is seen to be compounded of two normal effects, the one deriving from the shift of the equilibrium: $\text{Br}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{Br}^- + \text{HOBr}$ with temperature, and the other being the effect of temperature on the rate determining process: $\text{HC}_2\text{O}_4^- + \text{HOBr} \rightarrow 2\text{CO}_2 + \text{Br}^- + \text{H}_2\text{O}$. In the case of

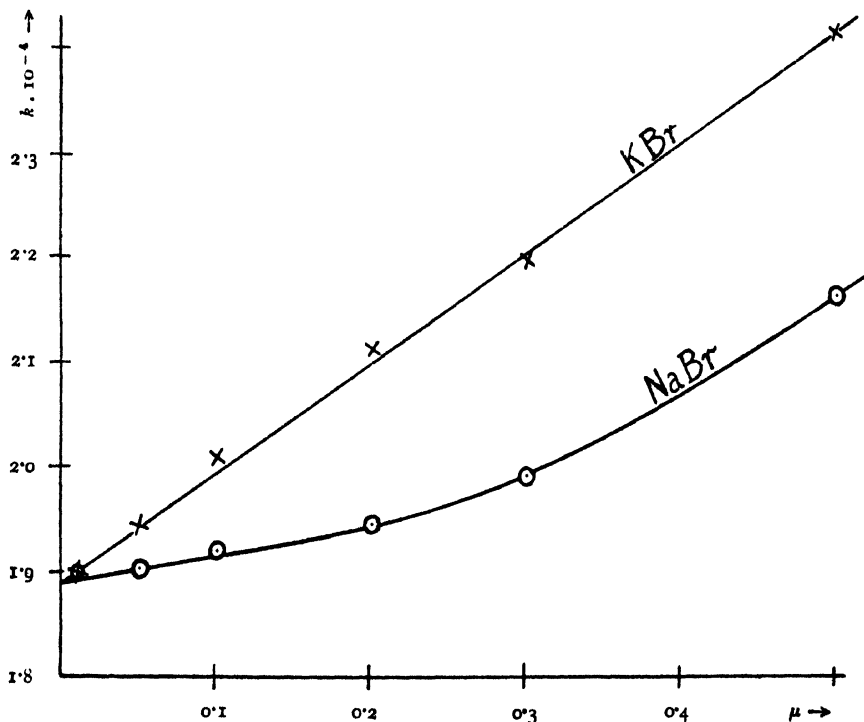
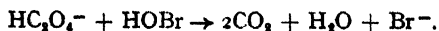


FIG. 4.

the constant kK/K_2 for the reaction between bromine and oxalates the temperature coefficient of K_2 is also included in the observed temperature coefficient.

Summary.

The thermal reaction between bromine and oxalic acid, acid-oxalates, and neutral oxalates in aqueous solution in presence of bromides and HBr has been studied at the three temperatures 11.5° , 16.5° , and 21.5° . The process which under all conditions determines the observed rate of reaction is:



The kinetic equations evolving from the mechanism have been integrated, enabling two series of constants kK/K_2 and kK to be evaluated. The ratio

of these gives K_2 , the second ionisation constant of oxalic acid; this is found to increase with increasing ionic strength (μ) of the solution. The constant kK also increases markedly with increasing μ ; it is shown that this is due to a large increase of K (the hydrolytic constant of bromine) with μ , together with a small (practically linear) increase of k (the velocity constant of the rate-determining reaction) with μ . Sodium and potassium bromides exert specific effects on K , K_2 , and k . The temperature coefficient of the reaction is of the order 6; an explanation of this unusually high value is given.

The authors desire to express their indebtedness to Imperial Chemical Industries, Ltd., for a grant defraying part of the cost of this work, and to the Department of Scientific and Industrial Research for a maintenance grant to one of them (A. G. W.).

*Muspratt Laboratory of Physical and Electrochemistry,
University of Liverpool.*

REVIEWS OF BOOKS.

Colloid Aspects of Food Chemistry and Technology. By WILLIAM CLAYTON, D.Sc. (Liverpool), F.I.C. (London. Pp. viii + 571 + xxiii. Price 36s. net.)

Whatever the reader's previous opinion on the commercial value of the study of the colloidal state, he cannot fail to be impressed by its wide applicability in food technology, and no worker connected with this industry can afford to be ignorant of the broad principles governing colloidal problems. The author has assumed an elementary knowledge of colloid chemistry, but nevertheless has given a brief introductory chapter on colloid chemistry and throughout the text deals in a simple and concise manner with the more well-known theories and conceptions, such as Loeb's theory of protein behaviour, Donnan's theory of membrane equilibria, the Proctor-Wilson theory of swelling of gelatin gels, Michaelis isoelectric point theory, the *Zwitterion* theory, the adsorption isotherm, together with a review of the literature on the structure of gels and the theories of emulsification, although the micelle theory appears to be accepted without explanation as to whether Duclaux's or McBain's conception is intended. The Glossary of Terms at the end of the book should be useful to students and to food chemists, who have lost touch with colloid principles.

The scope of the book has been declared in the preface thus: "It is not a treatise on food technology, but rather an introductory guide to aspects and problems of a colloid nature which may be unfamiliar to the food chemist." This limitation is probably necessary in order to keep the book within a reasonable size, but the reviewer feels that it is a pity that in some instances rather more references to actual practice were not given; when differences of opinion exist, a direction as to the consensus of opinion at the present time would be valuable to the chemist who has not specialised in colloid chemistry. Thus, in the discussion on agar-agar and gums, which find many uses in the food industries, little space is given to relationships between colloidal properties and suitability for commercial use; the methods for the purification of agar for bacteriological purposes are given, but no recommendations as to choice of method; again various methods of preparing ash-free gelatin are discussed but no critical advice is given. A general review on starch gelatinisation does not

include any indication as to whether the evidence available supports a definite temperature or a gradual process of gelatinisation. The importance in food technology of jelly strength is emphasised, but no practical experience is available to the reader, and, in the reviewer's opinion, a brief, critical examination of methods of the determination of gel strength would have enhanced the value of the book to the food industry. The change in starch viscosity under the influence of acid, processing and time is a practical problem in sauce manufacture, but no application of theory to practice is attempted. In the discussion on emulsions, however, many more references to actual practice in food technology are given and the reader feels that the author is giving his own personal experience more freely; thus in the case of butter, the statement is made that the Foam theory of butter making is supported by practical experience; again, the separation and whipping of cream are discussed in some detail both from the theoretical and from the practical standpoints. Similarly the subjects of "milk-froth" and homogenisation and the manufacture of cheese receive attention and technical consideration. The application of colloid principles in Sugar Technology and a review of technical operations are given, together with a consideration of the adsorption of colour from solutions. An interesting paragraph has been included dealing with the commercial applications of colloidal data to the manufacture of fruit jellies, jams, and marmalades.

The author has given on a number of problems his valuable opinion as to channels in which profitable research could be directed. Thus, the relation of moisture and temperature to plasticity of certain gums offers scope for research and, amongst technical emulsions, problems requiring elucidation are mentioned—the type of emulsion represented in a margarine, the emulsifiability of oils with different emulsifying agents, effect of ordered agitation on oil separation, the suitability of emulsions for processes of metabolism, the physico-chemical factors concerned in cream as an emulsion, and the effect of freezing on prepared emulsions.

The statement is made that agar is used in bread to inhibit staling; the reviewer has never met this in his experience and it is certainly not used very widely for this purpose in England. On page 146, appears the following: ". . . for the present, loaf volume seems the safest guide to the baking quality of a flour from the commercial standpoint." The reviewer disagrees with this; loaf volumes, particularly of tin bread, are very much in the hands of the baker and are influenced appreciably by baking conditions, so that very misleading conclusions can be drawn and, further, the commercial baker is more interested in the working of his dough than in the final volume of the loaf.

Discussing the viscosity of flour suspensions, the author says: ". . . it is usual to determine the viscosity of flour-in-water systems, not on the suspension itself, but on the residual suspension after appropriate extraction with distilled water." Although much work on these lines has been carried out in America, many cereal chemists take the view that, as the aqueous extracts remove electrolytes and some of the proteins, the viscosity figures thus obtained do not necessarily portray the properties of the actual dough system. The author has explained in full the " δ " factor of Gortner, but more recent work has failed to substantiate the value of this. No reference has been made in the text to the effects of heat on flour, which have recently been investigated by a number of workers in this field. Further, it is known in the trade that very small quantities of certain chemical substances can produce marked modification in the dough properties; this fact certainly deserves mention when considering the colloidal aspects of flour and dough. On page 154 it is definitely intimated that starch *does* influence flour strength, but no reasons are made available in support of this contention.

The book is well printed and attractively produced, although a number of typographical errors are to be found. It is a pity that uniformity was not maintained throughout with respect to the tables; some are numbered but not all, and again only a proportion of them are given titles. The two forms "micellæ" and "micelles" have been used without any stated differentiation (p. 99). These are only minor points and do not virtually detract from the value of the book, which should prove useful to all chemists and technologists in the food industry. The Bibliography is extensive and conveniently arranged under subject headings; owing to the wide range of subjects covered, it would be surprising if some omissions were not detectable and therefore the present reviewer does not propose to make suggestions thereon.

C. W. H.

Colloids. By ERNEST S. HEDGES, M.Sc., Ph.D., D.Sc. (London: Edward Arnold & Co., 1931. Pp. vii + 272. Price 12s. 6d. net.)

The author says in his preface: "For some years I delivered courses of lectures on Colloid Chemistry at Bedford College, University of London, and my students repeatedly asked me to write a non-mathematical text-book of colloids. I have adhered to this request as far as possible, and whilst the book has been written more especially for students of chemistry I have endeavoured to treat the matter in a sufficiently broad way to interest students of physics, biology and geology."

The book may be said to achieve its object. The arrangement adopted is one which the reviewer has always considered the proper one for—at least—an elementary text-book: the general characteristics of colloid systems are described before adsorption is treated in detail. An extremely brief chapter is devoted to emulsions, which their great and increasing technical importance might have entitled to fuller consideration, although the particle sizes even in the most highly disperse technical products hardly fall within the colloidal range.

As stated in the preface, the author devotes a larger portion of his space than is usual in text-books—46 pages out of 272—to the properties of gels. The reviewer agrees that this course is justified by the intrinsic interest of these systems and by the important part they play in organisms. He doubts, however, whether it is desirable on pedagogic grounds that half this space should be taken up by a chapter on reactions and periodic phenomena in gels, at any rate in an elementary text-book. The Liesegang phenomenon has a fascination for students out of all proportion to its importance (much overrated in the early years after its discovery) or to any benefit which they can derive from its study, and they should not be encouraged in this attitude.

In other respects the balance is satisfactory and more attention is given to facts and phenomena than to theory or "theories." The style is easy and the book should prove useful to the class of readers for whom it is primarily intended.

E. H.

THE ADSORPTION OF GASES BY SOLIDS.

A GENERAL DISCUSSION.

THE FIFTY-SIXTH GENERAL DISCUSSION organised by the FARADAY SOCIETY was devoted to "THE ADSORPTION OF GASES BY SOLIDS."

The meeting was held in the Lecture Theatre of the Biochemical Laboratory of the University of Oxford on Tuesday and Wednesday, 12th and 13th January, 1932, the President of the Society (Dr. Robert L. Mond) occupying the chair.

The subject was discussed in three sessions, following a General Introduction by Professor H. S. Taylor of *Princeton*, as follows:—

Part I. Experimental Methods. The Introduction to this Section was given by Professor E. K. Rideal, *Cambridge*.

Part II. Kinetics and Energetics was discussed on the afternoon of 12th January and in the morning of the 13th January. The Introductory Paper was written by Professor H. Freundlich, *Berlin*.

Part III. Theories of Adsorption was discussed on the afternoon of 13th January, the Introductory Paper being written by Professor M. Polanyi, *Berlin*.

On Monday evening, the 11th January, the President entertained the overseas members and visitors to dinner at the Dorchester Hotel, London. In addition to the President's English guests, the following were welcomed to England: Professor Arthur F. Benton (*Virginia*), Professor R. Marshall Chadwell (*Massachusetts*), Professor H. Jermain Creighton (*Swarthmore*), Dr. H. Dohse (*Ludwigshafen a. Rh.*), Professor G. Drucker (*Leipzig*), Dr. A. Farkas (*Frankfurt a. M.*), Dr. E. Hückel (*Stuttgart*), Professor A. Magnus (*Frankfurt a. M.*), Dr. C. Schuster (*Ludwigshafen a. R.*), and Professor H. S. Taylor (*Princeton*). During the evening letters of greeting to absent colleagues were signed by all present and despatched.

By the courtesy of the Master and Fellows of Balliol College, Oxford, the main body of members and visitors were given accommodation in that College for the period of the meeting, though many of those attending stayed with friends in Oxford. An informal dinner of the Society was held in the Hall on the evening of 12th January, when the Master of Balliol honoured the Society by presiding; 100 members and visitors were present.

The meetings were held in the Biochemical Theatre by the courtesy of Professor R. A. Peters and Sir Charles Sherrington; through the kindness of Professor Peters and his staff, tea was provided during the afternoon sessions in adjoining rooms.

At the opening session (at which there were about 170 present) the President welcomed particularly the overseas members and guests who had come to Oxford, and introduced them personally to the meeting. He expressed the regret which all felt at the absence of Professors Bonhoeffer, Freundlich, Mark, Polanyi, and Volmer, who had been prevented at the last moment from coming to England.

The papers had been issued in advance to those present, and were all taken as read. The authors were invited to open the discussion on their papers as they were reached in the fulfilment of the programme. As a result of this procedure a lively Discussion (which is reported in the succeeding pages) arose on the majority of the contributions.

In accordance with the wishes of the meeting, voiced by Professor Donnan, Professor J. E. Lennard-Jones was invited to summarise his paper from Section III. during the early part of the discussion of Section I., in order that those present might bear that paper in mind throughout the Discussion. Professor Lennard-Jones' paper is, however, printed in the succeeding pages under Section III. (Theories of Adsorption).

At the conclusion of the Meeting votes of thanks, moved by the President, were accorded with acclamation to the Overseas Guests for their presence, to the authors of papers and to contributors to the Discussion, to the Master and Fellows of Balliol, to Sir Charles Sherrington and to Professor Peters and his staff, and to the Organising Committee, and in particular to Professor Taylor, on whose initiative the meeting arose, and to Mr. O. Gatty, who had made arrangements for hospitality in Oxford. Finally, Professor Taylor thanked the President, first on behalf of the overseas guests for the munificent hospitality which he had accorded them, and then on behalf of all present for his sympathetic and business-like conduct of the meeting from the chair.

THE ADSORPTION OF GASES BY SOLIDS.

A GENERAL DISCUSSION.

GENERAL INTRODUCTION.

BY HUGH S. TAYLOR.

Received 24th December, 1931.

It is eminently fitting at a time when so much attention is being paid to the fundamental contributions of Faraday to electrical science that the Society which bears its honoured name should also devote some thought and discussion to a field of knowledge in which Faraday displayed the same qualities of genius and pre-vision that have given him so pre-eminent a position among the leaders of scientific thought. Faraday's contributions to the problem of adsorption were as conspicuously in advance of his time as were his discoveries in other fields of work. They are apt to be overlooked in modern presentations of the subject. And yet Faraday realised from his studies of reactions of hydrogen and oxygen at the surface of platina plates that the phenomena are

“dependent upon the natural conditions of gaseous elasticity combined with the exertion of that attractive force possessed by many bodies, especially those which are solid, in an eminent degree and probably belonging to all; by which they are drawn into association more or less close, without at the same time undergoing chemical combination, though often assuming the condition of adhesion; and which occasionally leads, under very favourable circumstances, as in the present instance, to the combination of bodies simultaneously subjected to this attraction.”

His studies of the inhibitory action of other gases on the process leading to his observation that

“the very power which causes the combination of oxygen and hydrogen is competent under the usual casual exposure of platina, to condense extraneous matters upon its surface, which soiling it, take away for the time its power of combining with oxygen and hydrogen, by preventing their contact with it,”

are the pioneering efforts in the field of specific adsorption at surfaces which have reached their culmination in the Langmuir concept of unimolecular adsorption and the consequent modern interpretation of chemical reactions at surfaces.

Faraday's emphasis on the “*superficial* actions of matter” became overlaid by the considerations of “porosity” in connection with the properties of adsorbent materials. There emerged the hypothesis

of *capillary condensation* which accounted for the observed adsorption in terms of liquid condensed in pores of the solid owing to the lowering of vapour pressure caused by surface tension effects. Adsorption at plane surfaces should be impossible on this basis, nor should gases be adsorbed at temperatures above the critical temperatures. Nevertheless in spite of much argument to the contrary, this "pore" concept still persists in certain quarters. It undoubtedly is of importance with saturated vapours as the gas phase. For adsorption on plane surfaces two rival points have struggled for supremacy. Since the time of de Saussure (1814) it has been assumed that adsorption occurred in *thick compressed films* the existence of which was to be associated with long range forces of attraction extending outwards from the solid surface with progressively diminishing potential. It was by diffusion through such thick layers of adsorbed gas that Bodenstein, Fink, Stock, and others assumed that reacting gases in heterogeneous gas reactions reached a reaction surface on which the velocity of interaction was relatively rapid. Langmuir, in 1915, emphasising the unsaturated nature of surface atoms in a solid lattice (the Braggs) and, at the same time, the extremely short range of inter-atomic and molecular forces simultaneously provided adsorption with the "*unimolecular adsorption layer*" and the heterogeneous reactions with a kinetics based on the extent to which a surface is bare or covered with unimolecular layers of adsorbed gas. So far as kinetics is concerned, acceptance of the Langmuir concept may be characterised as universal. As to adsorption, one can summarise the situation by saying that the thick compressed film has during the last decade become progressively thinner until now the tendency is to reinterpret the ideas of the compressed film in terms of the unimolecular layer.¹

Adsorption and Concentration.

The connection between extent of adsorption and the concentration (pressure) of the gaseous adsorbate at constant temperature is one of the most characteristic marks of adsorption. The relationship is frequently expressed by the equation,

$$x/m = kp^{1/n},$$

where x is the amount adsorbed by m grams of adsorbent, k is a constant, p the pressure of gas, and n a number which may vary from $n = 1$ to $n = \infty$. Over a limited pressure range a value for n may be found which adequately expresses the experimental results. Over a large pressure range this is not so, in which case an equation derived by Langmuir for a uniform surface on the basis of his concept of unimolecular adsorption may often be substituted. This equation takes the form

$$\frac{x}{m} = \frac{k'bp}{1 + bp}$$

where k' and b are constants, the other symbols having the significance given above. This equation will be seen to yield a value of $n = 1$ for low values of p ($bp \ll 1$) and $n = \infty$ for large pressures, in formal agreement with the classical expression above. It therefore indicates an adsorption proportional to the pressure for low pressures and an in-

¹ Cf. Polanyi, *Z. physik. Chem.*, **132**, 321, 371, 1928.

dependence of pressure (saturation of the surface) at sufficiently high pressures.

These equations are characteristic of adsorption in that, of the other possible processes that might occur, the one, solution, is governed by the relation $x/m = kp$ otherwise known as Henry's Law;² the other, compound formation between solid and gas, requires that below a certain pressure at a given temperature, no interaction occurs whilst, at this pressure, reaction goes to completion without further change in pressure. The continuous variation of the adsorption with pressure and the continuous variation of the exponent of the pressure with increased adsorption constitute, therefore, together, a decisive criterion of adsorption.

Non-Uniform Surfaces.

The Langmuir isotherm given represents an equilibrium between condensation of gas molecules on a uniform surface and their evaporation from the surface. The rate of condensation per gram of surface is obviously proportional to the pressure and the bare surface $(1 - \sigma)$

$$+ dx/dt = k_1 p(1 - \sigma).$$

The evaporation is proportional to the fraction of the surface of the area covered (σ)

$$\begin{aligned} & - dx/dt = k_2 \sigma \\ \text{At equilibrium} & + dx/dt = - dx/dt \\ \text{or} & k_1 p(1 - \sigma) = k_2 \sigma \\ \text{whence} & \end{aligned}$$

$$\sigma = \frac{k_1 p}{k_2 + k_1 p},$$

or since

$$\begin{aligned} \sigma &= k \cdot x/m, \\ x/m &= \frac{k' b p}{1 + b p}. \end{aligned}$$

The evaporation process varies exponentially with temperature,

$$k_2 = a e^{-\lambda/RT},$$

where a is a constant and λ is the heat of vaporisation (adsorption) which is constant for a uniform surface. For a non-uniform surface in which, on different fractional areas $\sigma_1, \sigma_2 \dots \sigma_n$ the heats of vaporisation are respectively, $\lambda_1, \lambda_2 \dots \lambda_n$ the number of molecules leaving the surface per unit time is a more complex quantity of the form

$$- dx/dt = a_1 \sigma_1 e^{-\lambda_1/RT} + a_2 \sigma_2 e^{-\lambda_2/RT} + \dots + a_n \sigma_n e^{-\lambda_n/RT}.$$

The implications of such an equation can be understood if one thinks of a surface composite of two types of equal areas but with different

² Provided no change in molecular state occurs in solution. If association occur then $x/m = kp^n$ where n is the degree of association. If dissociation occur (e.g., of a diatomic molecule into atoms) $x/m = kp^{1/n}$ where n is the number of dissociation products from one molecule of gas. This last equation differs from the adsorption equation in that n would not vary continuously, as in adsorption, up to large values with increasing saturation. For dissociation in solution becoming progressively less with saturation n would decrease to a final value of unity.

heats of vaporisation λ_1 and λ_2 . Since the areas are equal the condensation process will occur at the same rate on each area. The evaporation processes will be however different and given by the two expressions

$$a_1\sigma_1e^{-\lambda_1/RT} \quad \text{and} \quad a_2\sigma_2e^{-\lambda_2/RT}.$$

There is good reason to believe that $a_1 = a_2$ hence the rates of evaporation from the two equal areas covered will be in the ratio

$$e^{-\lambda_1/RT}/e^{-\lambda_2/RT} = e^{-(\lambda_1-\lambda_2)/RT}.$$

Let us assume for example that

$$(\lambda_1 - \lambda_2)/RT = 5,$$

that is to say the heats of evaporation differ by 3000 calories when $T = 300^\circ \text{K}$. Then the ratio of the rates of evaporation from equal areas covered will be $e^{-5} : 1$ or $1 : 150$ approximately. That is to say, at a gas pressure p at which the area with the larger heat of vaporisation is covered the second area will on the average be covered to the extent of 1 part in 150 that is, it will be relatively bare. The isotherm would be discontinuous, showing at the pressure in question a region of small change in adsorption with increase in pressure until the first area was covered followed by a second section at higher pressures corresponding to the filling of the area with lower heat of vaporisation. For more complex non-uniform surfaces the isotherm would reveal correspondingly more discontinuities. It is worth discussing whether the recent results of Allmand and Burrage² and of Benton and White⁴ are not entirely to be attributed to the operation of such factors, and it is a problem for further experimental enquiry whether such discontinuous isotherms are not to be quite generally found. Benton and White⁴ have formulated a specialised interpretation of such discontinuities. An alternative discussion of this point is given by Polanyi in this Discussion.

The measurements of heats of adsorption at various surfaces reveal quite generally the non-uniformity of the adsorbing surface. The initial areas covered are in general associated with high heats of adsorption. A progressive decrease in heat of adsorption occurs with increase of area covered. For a non-uniform surface, with sufficiently accurate measurements, this decrease should be stepwise. This of necessity involves discontinuity in the isotherms when examined over sufficiently small pressure ranges. The more varied the surface the less pronounced will be the discontinuities, since with minor differences in heats of adsorption (vaporisation), the less active areas will begin to fill with gas before the more active areas are completely filled.

In this question of the heterogeneity of surfaces the decisive contributions from studies of "poisoning" in chemical reactions occurring at surfaces must not be forgotten. They have served to emphasise not only the theoretical but practical importance of the non-uniform surface.

Mobility of Adsorbed Gases.

The brilliant experimental investigations of Volmer and his collaborators served to show that an adsorption layer on a surface might be extremely mobile and that the transfer of matter via such a mobile adsorbed film might be as much as 18,000 times greater than that occurring

² *Proc. Roy. Soc.*, **130A**, 610, 1931.

⁴ *J. Am. Chem. Soc.*, **53**, 2807, 3301, 1931.

through free evaporation into the air. This mobility effectively provides a mechanism whereby the areas of a surface having the highest heats of adsorption become covered with adsorbed gases before the surfaces of lesser activity.⁵ The saturation of such areas does not need to be attained by condensation processes alone but may be assisted by this two-dimensional motion parallel to the surface. It is a probable assumption that the mobility of adsorbed gases will be correspondingly less on the areas of stronger binding energies. Indeed, there is reason to believe that the two-dimensional motion may be limited to adsorption processes involving only the van der Waals' forces and that polar binding to the surface entirely suppresses any lateral motion. Experimental examination of this question of mobility in relation to the nature of the binding forces is an important current problem.

In this respect a recent study by Kautsky⁶ of hydrogenation of methylene blue at platinum areas sparingly distributed over surfaces of silica and thoria gels, is of great interest. Polar adsorption of the dye-stuff by the thoria restricted its access to the platinum centres and so slowed down hydrogenation in comparison with the velocity when silica was used as the platinum support. Silica does not adsorb the dyestuff in a polar manner. The conclusion is compelling that the material hydrogenated reached the platinum from the solution, not by lateral diffusion along the surface of the support-material when adsorbed by polar forces.

Nature of the Adsorption Process.

In what has preceded it has been tacitly assumed that only one adsorption process is occurring with a given gas and a given surface. Evidence is accumulating rapidly that this is not necessarily universally true. Even in the older literature there is sporadic evidence that more than one type of binding may be involved in an association of gas and surface. Dewar showed that the adsorption of oxygen on charcoal at liquid air temperatures involved a heat of binding of 3744 calories and that the oxygen was readily recoverable by pumping. At 0° C., Keyes and Marshall found a heat of adsorption of 72,000 calories for the first gas adsorbed and a difficult recovery mainly as oxides of carbon. Langmuir found that carbon monoxide was adsorbed by platinum and readily removed at liquid air temperatures, but was relatively irreversibly adsorbed at room temperatures and higher. Langmuir also found that the amount of oxygen adsorbed at liquid air temperatures by platinum was only one-tenth of that at room temperatures and that adsorbed in the higher temperature range is only removable by reaction with other gases. Benton and White have shown similar behaviour with hydrogen on copper and nickel, the low temperature adsorption being small and involving low binding energy, the high temperatures being greater and involving high heats of adsorption. The same is true for carbon monoxide on palladium (Taylor and McKinney) for hydrogen and for carbon monoxide on zinc chromium oxides (Garner and Kingman), manganous and manganous chromium oxides (Taylor

⁵ For a summary of this work see Volmer, this Discussion; Taylor, *Treatise of Physical Chemistry*, Vol. 2, pages 1063, 1074, Macmillan & Co., London; D. van Nostrand Co., New York; McBain, *Sorption of Gases and Vapours by Solids*, Chap. XI., Routledge, London, 1931. See also Bangham and Fakoury, *J. Chem. Soc.*, 1324, 1931.

⁶ *Ber. d. chem. Ges.*, 64, 2446, 1931.

and Williamson), zinc oxide (Taylor and Sickmann). In these latter cases the low temperature heats of adsorption are of the order 1-2 Kg. Cals. while the high temperature binding is about 20 Kg. Cals.⁷ Benton also in his communication to the present meeting lists other cases of this kind, of which a striking case is that of carbon monoxide on copper. At liquid air temperatures the adsorptions of nitrogen and carbon monoxide are of the same order of magnitude but at -78° and 0° the adsorptions of the latter are one or two orders of magnitude higher than those of nitrogen.

Activated Adsorption.

About a year ago the present writer⁸ called attention to the experimental fact that these high temperature adsorptions of gases with high binding energies were also processes occurring with measurable velocities. Furthermore, the velocities increased with increase of temperature in a manner familiar to students of chemical kinetics, the adsorption process occurring as though it involved an activation energy. For this reason this type of adsorption was designated "activated adsorption." It was shown that the concept of activation energy for such adsorption at once provided an explanation for the absence of such adsorptions at low temperatures, the temperature at which the activated adsorption becomes manifest being a function of the magnitude of the activation energy and characteristic for a particular surface—gas mixture. Thus, with hydrogen and the metals copper and nickel, activated adsorption sets in around liquid air temperatures. With zinc oxide, manganous oxide, and mixtures of these with chromium oxide activated adsorption of hydrogen becomes measurable in the interval 0° - 100° C. With alumina and glass such activated adsorption of hydrogen is not manifest until temperatures in the neighbourhood of 400° C. are reached. In another paper in this symposium the concordance between activated adsorption of hydrogen and the capacity of surfaces to induce the parahydrogen conversion is emphasised.

This extraordinarily simple generalisation of actual experimental observations seems to have aroused a quite unreasonable amount of opposition. Actually the concept of activated adsorption only generalises a number of independent and hitherto isolated experimental observations. By some the time-process has been interpreted to be exclusively one of solution of the gas in the metal.⁹ Benton has,⁸ in his communication to the symposium, shown that this is certainly not wholly tenable although no one will deny that some solution of these gases does occur in these metals. What the present writer would emphasise, however, is that for *all* cases where available data for the

⁷ It is unfortunate that, on the basis of data by Garner and Kingman it is being assumed that these adsorptions of hydrogen and carbon monoxide by oxides such as zinc chromium oxide involve interaction with the oxides at high temperatures with production of carbon dioxide or water. On the surfaces of zinc chromium oxide free from adsorbed oxygen both hydrogen and carbon monoxide can be adsorbed with high binding energies (20 Kg. Cals.) but recovered unchanged by evacuation at higher temperatures as hydrogen and carbon monoxide respectively. Moreover these reversible adsorptions obey all the criteria of adsorption, *e.g.*, obedience to the Langmuir isotherm (*cf.* Taylor and Williamson, "Adsorption of H_2 on the $MnO-Cr_2O_3$ at 305° and 444° C.," *J. Am. Chem. Soc.*, **53**, 2174, 1931).

⁸ *J. Am. Chem. Soc.*, **52**, 5298, 1930; **53**, 578, 1931.

⁹ Steacie, *J. phys. Chem.*, **35**, 2112, 1931; Ward, *Proc. Roy. Soc.*, **133A**, 506, 522, 1931.

classical investigations of solubility of gases in metals (*e.g.* those of Sieverts) overlap the determinations of activated adsorption, the solubilities in question in no single case amount to 5 per cent. of the measured adsorptions. This is a result diametrically opposite to that reached by Steacie in this regard. Well-investigated data in this matter are cited in the discussion of Ward's paper in the present discussion. The available data on the variation of activated adsorption with pressure also obey excellently the expression for the adsorption isotherm, a criterion for surface phenomena which we have already discussed. Did a solution phenomenon obey such a pressure relation the applicability of the Nernst Distribution Law to such a system would yield a peculiar and hitherto unknown distribution ratio. The obedience of the isotherms to an adsorption formula is equally strong evidence against this time process of adsorption being a compound formation involving the whole mass. A restriction of compound formation to the surface areas would produce the observed isotherms. A distinction between strong adsorption and surface compound formation is, however, merely a matter of expression and involves no fundamental difference in principle.

The experimental evidence with respect to velocity of adsorption is now sufficiently good that a decision can be reached as to the method whereby the adsorbed gas receives the activation energy required for the activated adsorption. Thus, data of Taylor and Sickmann on the adsorption of hydrogen by zinc oxide at 184° C. indicate that, on 20 grams of the oxide, 7.7 c.c. of hydrogen measured at N.T.P. were adsorbed in one hour, the activation energy of the process (deduced from the temperature coefficient in the range 132° to 184° C.) amounting to some 13,500 calories per mol. It is quite evident from a simple calculation that this adsorption is *not* to be accounted for on the assumption that adsorption occurs when gas molecules with an energy equal to 13,500 calories per mol. strike the surface. Kinetic theory teaches that the number of such molecules striking the surface per unit area per second is approximately

$$\frac{1}{4}(N/v)\bar{w}e^{-13500/RT}$$

where N/v is the number of molecules per c.c., \bar{w} the root mean square velocity of the molecules. For the case in point, this equation gives a value of $\frac{1}{4} \times 3 \times 10^{19} \times 2.5 \times 10^5 \times e^{-15} \times 60 \times 60$ molecules per sq. cm. per hour or approximately 2×10^{21} molecules *per square cm.* per hour. This is some ten times the amount actually taken up by the *whole* zinc oxide surface in the time interval in question. One must conclude, therefore, that the molecules receiving the necessary activation energy are first adsorbed on the surface and obtain the energy required from the surface. An enquiry into the manner in which such energy can be communication has recently been initiated by Herzfeld and Mrs. Mayer.¹⁰

Nature of Adsorption Forces in Normal and Activated Adsorption.

The development of the quantum-mechanical method of approach to physical and chemical problems has recently been extended by London to the problem of adsorption.¹¹ London has shown that by considera-

¹⁰ *Z. physik. Chem., Bodenstein Festband*, 1931.

¹¹ *Ibid.*, 11B, 222, 1930.

tion of the van der Waals' forces alone, it is possible to derive, quantum-mechanically, values for the heats of adsorption of non-specific adsorbates on charcoal surfaces in good agreement with experimental results.

For adsorptions with activation energies it is probable that the calculations involve not only the coulombic forces but also the non-classical interchange energies between atoms of adsorbent and adsorbate. The approach to the calculation of activation energies in such cases will probably follow the procedure used so successfully by Polanyi and Eyring in their treatment of the activation energies of chemical reactions.¹² An attempt to interpret activated adsorption along these lines is at present in progress in Princeton by Mr. A. Sherman under the guidance of Dr. Eyring. The problem under study is the calculation of the activation energy of hydrogen adsorption on charcoal surfaces. Only the preliminary results of such study are at present available, but these point to interesting conclusions with real significance not only in adsorption studies but also in respect to reactions at surfaces. Sherman's preliminary calculations indicate that the activated adsorption of hydrogen on a graphite surface with the normal carbon-carbon distance of 1.54 Å. would require an activation energy of about 50 Kg. Cals. owing to the operation of repulsive forces between the carbon and the hydrogen. If the carbon-carbon distance were very large, a large activation energy would also be required, although the repulsive energies between carbon and hydrogen would be small, because of the energy necessary to separate the hydrogen atoms to large distances. Between these, Sherman finds an "ideal" carbon-carbon distance such that neither controlling factor in the two previous cases is important with the result that the energy necessary to bring a hydrogen molecule up to the C-C pair is small. Actually with a C-C distance of about 2.4 Å. the activation energy has decreased to a value of about 5 Kg. Cals. While this must be regarded as only a preliminary survey of this interesting field it must be evident that its further exploration promises to be full of interest not only in the new field of activated adsorption which has just been opened up but also in the realm of reactions at surfaces where the evidence is already definite and compelling that the adsorptions involved in chemical reactions are activated in type.

*The University,
Manchester.*

¹² *Z. physik. Chem.*, **12B**, 279, 1931; *J. Am. Chem. Soc.*, **53**, 2537, 1931.

ON THE ADSORPTION OF GASES.

SECTION I. EXPERIMENTAL METHODS.

INTRODUCTORY PAPER TO SECTION I.

BY ERIC K. RIDEAL.

Received 19th December, 1931.

In an introductory paper it is impossible even to give a sketch of the enormous field embraced under the discussion. I have accordingly attempted to give in briefest outline only a short account of a few of the problems connected with the experimental investigation.

We may note as of primary importance, the determination of the specific surface of the adsorbent. In logical sequence we must examine the various methods which have been employed for the examination of the final distribution of the gas which has been sorbed, *i.e.*, between the surface and the bulk phase respectively. Examination of the rates of attainment of equilibrium involve the measurement both of the critical energy increments and the reaction velocities of the various processes taking place when a solid is exposed to a gas. Finally, we must mention the experimental methods which have been devised to examine in more detail the process of formation of surface phases.

The Specific Surface.

Of fundamental importance is the nature and extent of the surface phase of the solid. With the realisation of the somewhat porous structure of the surface layers of most solids, the evaluation of the accessible area rather than the true specific area has been more important. Some five methods have been employed for this purpose. These may be briefly enumerated as follows :—

(1) Comparison of the rate of solution in some reagent with that of a uniform surface of similar material, which is a method originally employed by Schmidt,¹ Wolff,² Durau³ and more recently by Schwab and Rudolph,⁴ for evaluation of the specific surface of reduced nickel. Lack of uniformity in the rate of solution is the chief objection to this method.

(2) By determination of the Newtonian "temper" colours developed by metals when attacked by reactive gases. From a knowledge of both the film thickness determined optically and either the increase in weight of the metal or the volume of gas which has been taken up by the

¹ Schmidt, *Z. physik. Chem.*, **118A**, 236, 1925.

² Wolff, *Z. angew. Chem.*, **35**, 138, 1922.

³ Durau, *Z. Physik*, **38**, 419, 1926.

⁴ Schwab and Rudolph, *Z. physik. Chem.*, **12B**, 427, 1931.

metal, the specific surface can be evaluated. This method has been employed both by Dunn⁵ and by Constable.⁶ Uniformity of film thickness and uniformity of composition of the film is, as observed by Evans,⁷ not readily obtainable, and all irregularities in the surface texture must be assumed to possess a substrate thickness at least equal to that of the resulting film.

(3) The change in electrode potential caused by the passage of a definite electric flux 6.010^6 coulombs per sq. cm. for a 100 mv. change in interface potential across a liquid metal interface, permits of the evaluation of the specific surface. This method was developed by Bowden and Rideal,⁸ and has been used by Bowden⁹ and by Volmer and Erdly Griz.¹⁰ A theoretical treatment of the method on the basis of the wave mechanics has recently been given by Gurney.¹¹

(4) The fact that the conditions of reversible adsorptive equilibrium are quickly established between the surface of an insoluble salt such as lead sulphate and a solution containing isotopic ions such as the radioactive thorium B, has been utilised by Paneth and his co-workers¹² to evaluate the specific surface of such salts, and by Hahn.¹³

(5) A number of investigators have attempted to evaluate specific surfaces from experimental data on the adsorption of solutes which are readily quantitatively determined in small quantities. It is assumed in all cases that the saturation maximum corresponds with a close packed unimolecular layer. Dyes estimatable by colorimetric methods have been employed by Paneth and Radu,¹⁴ by Bancroft and Barnett,¹⁵ and by Bancelin.¹⁶ Metallic ions such as silver determined by electropotentiometric methods have been utilised by Euler.¹⁷ The inapplicability of the former, even when not colloidal, to fine grained or porous materials, and of the latter to interfaces which in general possess a potential difference, e.g., mercury in a Lippmann electrometer to the exact determination of the specific surface, is clearly evident; the method although simple is very restricted in scope and the accuracy attainable very problematical.

After the evaluation of the specific surface of the solid the next problem which arises in the experimental investigation is the examination of the detailed molecular structure of the surface, this is necessary since the characteristics of the adsorption isotherms as well as the thermal changes appear to be dependent on the structure. It cannot be said that much progress has been made in this direction. We may note the attempts which have been made for the evaluation of the mean grain size when crystalline, utilising Debye's method of X-ray examination by Astbury and Clark,¹⁸ and by Feichtknecht¹⁹ and the more recent ex-

⁵ Dunn, *P.R.S.*, **101A**, 203, 1926.

⁶ Constable, *P.R.S.*, **117A**, 376, 1928; **119**, 196, 1928.

⁷ Evans and Bannister, *P.R.S.*, **125A**, 370, 1929.

⁸ Bowden and Rideal, *P.R.S.*, **120A**, 63, 1928.

⁹ Bowden, *P.R.S.*, **125A**, 446, 1929.

¹⁰ Volmer and Erdly Griz, *Z. physik. Chem.*, **150A**, 203, 1930.

¹¹ Gurney, *P.R.S.*, **134A**, 137, 1931.

¹² Paneth, *Z. physik. Chem.*, **101**, 445, 480, 1922; *Ber.*, **57B**, 1215, 1924.

¹³ Hahn, *Z. physik. Chem.*, **144A**, 161, 1929.

¹⁴ Paneth and Radu, *Ber.*, **57B**, 1221, 1924.

¹⁵ Bancroft and Barnett, *Coll. Symp.*, **6**, 73, 1928.

¹⁶ Bancelin, *J. Chim. Physique*, **22**, 522, 1925.

¹⁷ Euler, *Z. Elektrochem.*, **28**, 2, 1922.

¹⁸ Astbury and Clark, *J.A.C.S.*, **47**, 2261, 1925.

¹⁹ Feichtknecht, *Z. Elektrochem.*, **35**, 142, 1929.

periments of G. P. Thomson,²⁰ in interpreting the diffraction patterns obtained with high speed electrons.

The existence of a network postulated by Smekal²¹ and Lennard Jones and Dent,²² has been demonstrated by optical methods by Zwicky.²³

The problem of the surface structure is evidently capable of being attacked in an alternative manner not by analysis but by synthesis. By laying down a fresh surface *in vacuo* either as small aggregates in cathodic spluttering or molecularly by evaporation, its properties and the change of these properties on ageing and with time have been the subject of several investigations. We may mention the work of Estermann²⁴ on the growth of crystals of silver and cadmium deposited by molecular rays of these metals. Optical methods for the examination of the deposits have been developed by Reinders and Hamburger,²⁵ whilst the numerous observations on the change in electrical conductivity with age have been the subject of theoretical discussion by Frenkel²⁶ and Ehrenberg and Hönl.²⁷

The adsorptive powers of deposited films for various gases has been the subject of detailed investigations by Frankenburger and his co-workers.²⁸ The experiments of Bastow²⁹ on the sorption of nitrogen and hydrogen by deposited platinum are of interest in this connection.

The Surface Phase.

If a metal surface be exposed to a gas and sorption takes place, it is important to consider what experimental methods can be devised to discover whether the gas is retained on the surface of the metal or no. A number of such methods have in fact been employed and at least one of them has been found to be capable of yielding quantitative, as compared with qualitative, results as to the existence, extent and nature of the surface phase. We may briefly review these methods:—

(a) At high temperatures the thermionic emission from a clean surface is given by Richardson's equation $i = AT^2 e^{-\phi/KT}$. The work function ϕ is very considerably modified by the presence of foreign atoms in the surface phase. For dilute films this modification may be expressed in the form $\phi' = \phi + \alpha\theta$ where θ is the fraction of the surface covered with foreign atoms, α being either positive or negative. For surface concentrations of less than 10 per cent. in the case of caesium and for closely packed films, this simple expression is no longer valid. The method has been developed as a weapon for the examination of surface film structure, more especially by Langmuir, Becker, and Kingdon.³⁰ Whilst the method of examination by thermionic emission is naturally restricted to relatively high temperatures, the change in potential at a gas liquid interface caused by the insertion of a film can readily be measured at ordinary temperatures,³¹ and it has been found possible

²⁰ G. P. Thomson, *P.R.S.*, **133**, 1, 1931.

²¹ Smekal, *Physik. Z.*, **26**, 700, 1925; **45**, 869, 1927.

²² Lennard Jones and Dent, *P.R.S.*, **121A**, 247, 1928.

²³ Zwicky, *Proc. Nat. Acad. Sci.*, **15**, 253, 1929.

²⁴ Estermann, *Z. physik. Chem.*, **106**, 403, 1923; *Z. Physik.*, **33**, 320, 1925.

²⁵ Reinders and Hamburger, *Rec. Trav. Chim. Pays Bas*, **50**, 357, 475, 1931.

²⁶ Frenkel, *Physical Rev.*, **36**, 1604, 1930.

²⁷ Ehrenberg and Hönl, *Z. Physik*, **68**, 289, 1931.

²⁸ Frankenburger, *Z. Elektrochem.*, **35**, 920, 1929, *et seq.*

²⁹ Bastow, *J.C.S.*, 1931.

³⁰ Langmuir, Becker, and Kingdon, *see* Schottky, *Handbuch expt. Physik.*; Dushman, *Reviews of Modern Physics*, **2**, 381, 1930.

³¹ Schulman and Rideal, *P.R.S.*, **130A**, 259, 1931.

(unpublished work by H. Whalley) to extend this method to metal gas interfaces.

(b) The presence or absence of a surface phase can be demonstrated by the nature of the diffraction pattern obtained on reflection of electrons of relatively low velocities from metallic surfaces, a method due to Davisson and Germer,³² and extended very considerably by Rupp.³³ The necessity for high vacua precludes the methods from becoming a general one for the determination of the conditions of equilibrium. It may be noted in passing that the difficulties of obtaining a metal surface really free from gas is clearly demonstrated by this method of examination.

(c) Many attempts have been made to obtain information to the existence or absence of a surface film from an examination of the long wave threshold value of the photo-electric emission. Those of Ives³⁴ may be cited as an example of the method in its application to films of the alkali metals. The difficulties inherent in the method are great, and although as yet its general applicability must be considered restricted, it is a method worth further serious attention.

(d) The most suitable optical method at present available for the detection of a unimolecular film is that based upon the observations of Jamin³⁵ that plane polarised light when reflected from the surface of water was slightly elliptically polarised. The theoretical treatment by Drude (*Theory of Optics*) revealed on reflection of plane polarised light both the existence of a change in amplitude and in phase of the two component beams when there existed a transition layer or film of refractive index different from either medium. By suitable measurements it should be possible to obtain not only the film thickness and the refractive index but also the dispersion of the film forming material. It is possible that with the development of the theory of molecular scattering, the method may be capable of giving information on the electrical properties of the adsorbed phase. The most exhaustive examination of a surface phase by this method has been carried out by Tronstad on oxide films on metals. In all cases his films were relatively thick. Unimolecular films have been detected by numerous investigators and making assumptions which in some cases at least are somewhat unwarranted, molecular dimensions have been calculated from the observations.

The work of Sissingh and Haak³⁶ on mercury surfaces, of Ives and Johnson³⁷ on thin films of rubidium, of Frazer³⁸ on alcohol on glass, and of Bouchet,³⁹ may be mentioned as representative of the experimental methods employed.

(e) There are two thermal methods of investigation which appear to be capable of more precise development. The amount of energy carried away from a wire at a temperature T_2 by the impingement of molecules of a pure gas at a temperature T_1 on its surface is given by Knudsen's equation in the form $Q = K\alpha \frac{(T_2 - T_1)}{\sqrt{T_1}}$ where α is the accommodation co-

³² Davisson and Germer, *Physical Rev.*, **2**, 35, 705, 1927.

³³ Rupp, *Ann. Physik*, **5**, 453, 1930.

³⁴ Ives, *Physical Rev.*, **34**, 117, 1929.

³⁵ Jamin, *Jour. de Chem.*, **31**, 165, 1851.

³⁶ Sissingh and Haak, *P.R. Acad. Sci. Amst.*, **21**, 678, 1919.

³⁷ Ives and Johnson, *Proc. Opt. Soc.*, **15**, 374, 1927.

³⁸ Frazer, *Physical Rev.*, **33**, 47, 1929.

³⁹ Bouchet, *C.R.*, **185**, 200, 1927; and *J. Physique*, 1931.

efficient. The accommodation coefficient α is dependent on the nature of the surface. In the presence of an adsorbed layer of a foreign gas the value of α rises. The experimental work of Hughes and Bevan,⁴⁰ Chapman and Hall,⁴¹ Farkas,⁴² and especially the investigations of Roberts⁴³ may be cited as applications of the method.

Both the monochromatic as well as the total thermal emissivity of a surface is dependent on the nature of the surface. We may cite the values of the latter for (bright) platinum and oxidised platinum (black ?) from the I.C.T.

Temperature.	^{obs.} Pt	^{obs.} PtO.
400°	4.66	8.6
600°	7.50	11.0

Van Praagh and Rideal⁴⁴ found that the temperature of a tungsten wire maintained *in vacuo* varied for identical energy consumptions from 44° C. to 80° C., the latter in presence of a film of tungstic iodide on the surface computed to be ten molecules in thickness. A film this thickness still possessed the characteristic dissociation pressure of a bulk phase. The total emissivity is accordingly less for this film coated surface than for the bare metal.

It is possible that the change in emissivity caused by the presence of a unimolecular film is small,⁴⁵ and that the applicability of the method is restricted to thicker films.

The Bulk Phase.

The methods of examination available apart from those involving the measurement of velocities for the presence of the sorbed gas in the bulk phase of the adsorbent are somewhat less general than those described above for the detection in the surface phase. Whilst analytical methods present no difficulty, the distribution and state of the gas or vapour are not so readily discerned. We may divide the possible forms of distribution into the following: compound formation, lattice distribution, distribution in the slip planes and between the crystallites, distribution in micro-capillaries or channels. The increase in specific volume suffered by substances as varied as charcoal, metals such as palladium, platinum and iron, zeolites and clays, when sorption occurs is readily measurable,⁴⁶ but on account of the slow rate of attainment of true equilibrium the exact reversibility of the dimensional increase is difficult to demonstrate. Further expansion on sorption of gases has been demonstrated in the case of both platinum and palladium by means of the X-rays,⁴⁷ but as is well known the phase diagrams for these systems are still in an unsatisfactory state.

A few measurements have likewise been made of the change in electric resistance of wires on sorption and desorption of a gas.⁴⁸

⁴⁰ Hughes and Bevan, *P.R.S.*, 117A, 102, 1928.

⁴¹ Chapman and Hall, *ibid.*, 124A, 478, 1929.

⁴² Farkas, *Z. physik. Chem.*, 1931.

⁴³ Roberts, *P.R.S.*, 129A, 146, 1930.

⁴⁴ Van Praagh and Rideal, *P.R.S.*, 134, 400, 1931.

⁴⁵ *Loc. cit.*

See also Langmuir, *J.A.C.S.*, 38, 2271, 1916.

⁴⁶ *See* McBain, *The Sorption of Gases by Solids*.

⁴⁷ Handwalt, *Physical Rev.*, 33, 444, 1929; Osawa, *Tohoku Imp. Univ.*, 1, 14, 1925.

⁴⁸ Sieverts, *Z. Metallurg.* 3, 37, 1913.

Rates of Sorption.

Measurements of the rate of establishment of sorption equilibrium in themselves give but little information, unless the rates of the various processes taking place can be separately evaluated. It would appear that surface adsorption equilibrium is almost instantaneously attained. The adsorbed gas may now undergo further operations involving thermal changes; it may undergo reaction with the substrate to form a chemi-adsorptive compound, such a process requires an energy of activation and involves a thermal change. This phenomenon appears similar to, if not identical with, Taylor's hypothesis of activated adsorption. The adsorbed gas may penetrate into the substrate either along the intergranular boundaries or slip planes or possibly in the finer dimensions postulated by Smekal, or actually penetrate through the space lattice of the crystalline solid. It has been fairly definitely established that both these latter processes mimic ordinary chemical reactions, in that energies of activation are required for the diffusion processes and that these differ for the intergranular or slip plane and lattice diffusion processes respectively. Furthermore, the rate at which both these processes occur follows the ordinary Fick diffusion law in the sense that the rate of passage from the surface to the interior and in the opposite sense on desorption is dependent on the concentration gradient from the interior to the surface, the concentration at the surface being proportional to the amount of gas actually superficially adsorbed which is by no means necessarily proportional to the pressure of the gas. We may cite the experimental work of Langmuir⁴⁹ and Clausing,⁵⁰ on the migration of thorium through tungsten; of Dunn,⁵¹ Feichtnecht,⁵² and Wilkins and Rideal⁵³ on the diffusion of oxygen through copper oxide, and of Ward⁵⁴ on the diffusion of hydrogen through copper, as examples of direct measurement of rates of such diffusive processes and the determination of the critical energy increments.

Measurements of the rates and critical energy increments of the other possible reaction of the adsorbed gas, namely, conversion into a chemi-adsorptive compound, have generally been under conditions when the possibly important processes of intergranular and lattice diffusion have been ignored, nevertheless the existence of this transformation has been clearly demonstrated although the values given for the critical energy increments based upon the supposed rates may be somewhat inexact. We may cite the work of Garner and his co-workers on the adsorption of oxygen by charcoal,⁵⁵ and of Taylor and his colleagues on the adsorption of hydrogen by oxides.

We may note in passing that since the rate of the intergranular diffusion into a fully evacuated solid is governed by the amount of gas adsorbed on the surface and the texture of the surface, (*i.e.*, the number and size of the fissures), this rate may be very considerably affected by the presence of any substance sufficiently strongly adsorbed, which not only reduces the amount of gas adsorbed on the surface but may also reduce the number and size of the fissure entrances, this phenomenon is

⁴⁹ Langmuir, *Physic. Rev.*, **22**, 357, 1923.

⁵⁰ Clausing, *Physica*, **7**, 193, 1927.

⁵¹ Dunn, *P.R.S.*, **111**, 210, 1926.

⁵² Feichtnecht, *Z. Elektrochem.*, **35**, 142, 1929.

⁵³ Wilkins and Rideal, *P.R.S.*, **128**, 394, 1930.

⁵⁴ Ward, *P.R.S.*, **133**, 523, 1931.

⁵⁵ Garner, *J.C.S.*, **125**, 1288, 1924; 2451, 1927; 2870, 1928; *Nature*, **124**, 409, 1929.

exemplified in the work of Maxted on the influence of hydrogen sulphide on the rate of sorption of hydrogen by platinum.⁵⁶

Rates of Surface Migration.

We have already referred to the measurement of the rates of intergranular and lattice diffusion processes involved in the phenomenon of gaseous sorption and to the fact that adsorbed molecules may undergo reaction with the substrate to form a chemi-adsorptive compound. The chemi-adsorptive compound is presumably rigidly held on to the substrate surface and can only undergo lattice diffusion at elevated temperatures. We must examine the experimental methods for determining whether the adsorbed molecules are held in the sense that they perform oscillations within a small compass on the surface or whether they can migrate over the surface. Direct evidence for the lateral mobility of molecules moving over a substrate of the same material and of molecules moving over glass have been provided by actual visual and micro-balance observations by Volmer and his co-workers.⁵⁷

The movement of metallic atoms deposited on glass and on metal surfaces from beams of molecular rays has been directly observed by Estermann, by Stern,⁵⁸ and by Cockcroft.⁵⁹ Whilst the numerous examples of mobility at relatively low temperatures provided by the phenomenon of sintering are well known, Becker's⁶⁰ observations on the migration of the alkali metals and of the alkaline earths over platinum by observation of the change in the thermionic emission, likewise provide us with direct evidence on this point. The method of measurement of the change in the gas solid interfacial potential mentioned above is likewise capable of providing similar information as well as on the rates of formation and evaporation of surface phases at low temperatures.

A study of kinetics of the oxidation of copper⁶¹ provides us with indirect evidence for the lateral mobility of oxygen over copper oxide. The hypothesis of lateral mobility of adsorbed gases provides us with a very useful mechanism for the interpretation of surface actions,⁶² although if the activation process for a surface catalytic chemical reaction involves the activation of a chemi-adsorptive compound which by some is supposed to be the only species capable of entering into a subsequent chemical reaction, the hypothesis of lateral mobility of at least one of any two surface reacting gases must be given up.

A very brief consideration of the observed effect of temperature on these lateral velocities show that in general the rate of movement is not only far less than in the free gas phase at corresponding temperatures but, furthermore, possesses at least in the cases carefully examined on relatively clean and dry surfaces (*e.g.*, the experiments of Becker) a definite exponential temperature coefficient indicative of an energy of activation being requisite for the process of lateral diffusion, *i.e.*, in passing from point to point in a non-uniform atomic field. It is possible that this energy of activation for lateral diffusion may prove to be identical with the

⁵⁶ *J.C.S.*, 2203, 1931.

⁵⁷ Volmer, *e.g.*, *Z. Physik*, 35, 170, 1925; *Z. physik. Chem.*, 136, 183, 1928, *et seq.*

⁵⁸ Stern, *Z. physik. Chem.*, 106, 397, 1923; and 39, 774, 1926.

⁵⁹ Cockcroft, *P.R.S.*, 119A, 1928.

⁶⁰ Becker, *Trans. Amer. Electrochem. Soc.*, 1929.

⁶¹ Wilkins, *P.R.S.*, 178A, 407, 1930.

⁶² See especially Schwab, *Katalyse*.

value obtained for the process of diffusion in the intergranular boundaries and fissures of the solid. We may make an approximate calculation for this energy of activation of surface diffusion from Wilkins' experiments (*loc. cit.*) on the oxidation of copper. The rate of oxidation as determined by the rate of change of pressure at 500° K. at 300 mm. pressure was found to be 1.74 mm./sec. The area of the foil was 2 sq. cm. and the volume of the system about 100 c.c. Hence the rate of loss of oxygen into the interior was 0.115 c.c. (at N.T.P.) per sq. cm. per sec. At this pressure by the Herz Knudsen equation at least $3 \cdot 10^3$ c.c. would strike the surface per second. If free lateral mobility were possible for all atoms striking and the accommodation coefficient were unity on the oxide coated surface, it is clear that the limiting pressure observed, *viz.*, 300 mm. would be much less. If only a fraction $e^{-E/RT}$ of the condensing molecules acquire sufficient lateral mobility to migrate to a fissure we obtain $e^{-E/RT} = 0.115/3 \cdot 10^3$ whence $E = 12,400$ cal. per gm. mol. for the energy of activation for surface migration, a value not widely different to 9500 cal. for the energy of activation of the intergranular diffusion process.

In Davisson and Germer's experiments³² on adsorbed hydrogen films on nickel, the apparent "melting-point" of the film was found to be 400° K. If at this temperature the number of hydrogen atoms moving from point to point becomes so large that the electron diffraction pattern becomes too weak for observation we obtain the small value of $E = \text{Ca } 1000$ calories. The occlusion rate of hydrogen through nickel has been measured by Sieverts⁶³ who noted a rapid sorption above 200° C. It is an interesting speculation how far an atom can travel when once liberated in this manner, but the evidence provided by molecular ray experiments appears to indicate that the range of action when in the liberated state is small and that the molecule suffers rapid readhesion.

On Energy Exchange between Gas and Solid on Adsorption.

We have mentioned the experimental methods which have been devised to test the hypothesis that molecules impinging on a surface may condense and then undergo chemi-adsorptive reaction or pass into the interior via the intergranular channels or through the lattice.

When condensation does not occur the impinging molecule is reflected. The life of a molecule on the surface may thus be very short or very long; we may summarise the various experimental methods which have been devised to examine the result of collision of a molecule with a surface and the effect of increasing the lifetime of the molecule on the surface, *i.e.*, in altering the relative magnitudes of ϕ and kT . For extremely short lifetimes comparable with the lattice frequency (10^{-13} secs.) the interaction must be regarded as governed by the laws of wave mechanics. If the atoms are arranged in a regular lattice a certain proportion then are reflected or diffracted and for them there is no interchange of energy at all. We are indebted to Stern and Knauer,⁶⁴ Estermann and Stern,⁶⁵ and Johnson⁶⁶ for confirmation of the applicability of de Broglie's wave equation by the method of molecular rays.⁶⁷ In this case, as shown by Roberts,⁶⁸ the accommodation co-

⁶³ Sieverts, *Z. Elektrochem.*, **16**, 707, 1910.

⁶⁴ Stern and Knauer, *Z. Physik*, **53**, 779, 1929.

⁶⁵ Estermann and Stern, *Z. Physik*, **61**, 114, 1930.

⁶⁶ Johnson, *J. Franklin Inst.*, **206**, 308, 1928; **207**, 635, 1929; **210**, 145, 1930.

⁶⁷ *Molecular Rays*, 1931, Fraser, Cambridge Univ. Press.

⁶⁸ Roberts, *P.R.S.*, **129A**, 146, 1930.

efficients are small and the extent of this energy interchange is thus very small; an approximate theory of this case has been developed by Jackson. When the lifetime increases in this manner and the energy interchange becomes more pronounced the reflection becomes more and more diffuse as shown by the experiments of Langmuir,⁶⁹ Knudsen,⁷⁰ and Wood.⁷¹

With molecular rays the conditions for condensation can readily be examined and Frenkel's⁷² analysis tested. At the critical stream densities and temperatures the lives are naturally much greater than those obtained for specular reflection. Wertenstein,⁷³ by observation of the rate of condensation of mercury vapour on glass, obtained ca. 10^{-6} seconds at 300° K. Cockcroft⁷⁴ obtained 10^{-6} seconds at 250° K. for cadmium on copper. These lifetimes are all maximum values. When condensation occurs not only has thermal equilibrium with the surface taken place but the condensed atoms have reacted with one another to form a condensate. We may regard this phenomenon as the formation of a chemi-adsorptive compound with the substrate followed by activation and reaction with a neighbour. The importance of the lifetime on the surface as a factor in facilitating the transfer of energy is thus evident. The question of energy transfer in relationship to time of contact is clearly important in chemi-adsorptive reactions as the rate of transfer of kinetic energy of translation, of rotational energy and of internal vibrational energy may not be identical. That differences exist in the rate of transfer for the different kinds of energy in simple molecular collisions is apparent from the recent work of Kneser on carbon dioxide where a relaxation period of as long as 10^{-5} seconds was found for the transfer of the vibrational energy, whilst Herzfeld and Rice,⁷⁵ observed as a mean time for the transfer of rotational energy 10^{-8} seconds. We may note in this connection that Rice and Byck⁷⁶ obtained no signs of decomposition at a platinum target at 1600° C. of impinging beams of acetone or dimethyl mercury. In the latter case, if equipartition had been attained, with an energy of activation of 35,000 cal./gm. mol. over 6 per cent. decomposition should have been attained.

The same point may be demonstrated in another way. According to Taylor's values the energy of activation for chemi-adsorption of hydrogen on a metal is about 12,000 cal./gm. mol. Taking hydrogen at 100 mm. pressure 10^3 c.c. strike 1 sq. cm. of the surface per second according to the Herz Knudsen equation. If a fraction $e^{-E/RT}$ of these underwent the chemi-adsorptive reaction, reaction would be complete in about 10^{-5} seconds. If, on the other hand, the reaction be supposed to take place after adsorption and we consider N molecules adsorbed per sq. cm. at any time, the rate at which these enter into reaction will be $N\nu e^{-E/RT}$ where $1/\nu = \tau$ is this period of interchange. If we insert the ordinary vibration frequency $\tau = 10^{-13}$ in the above equation we obtain as rate of reaction $N \cdot 4 \cdot 10^6$, i.e., an extremely rapid rate of reaction. A value of $\nu = 10^6$ or $\tau = 10^{-6}$ seconds gives us a rate equal to 0.42, which if the surface is but sparsely covered is a measurable rate of reaction.

⁶⁹ Langmuir, *Proc. Nat. Acad. Sci.*, **141**, 1917.

⁷⁰ Knudsen, *Ann. Physik*, **48**, 1115, 1915.

⁷¹ Wood, *Phil. Mag.*, **30**, 300, 1915.

⁷² Frenkel, *Z. Physik*, **26**, 117, 1924.

⁷³ Wertenstein, *J. Physique*, **4**, 281, 1923.

⁷⁴ Cockcroft, *P.R.S.*, **119A**, 1928.

⁷⁵ Herzfeld and Rice, *Physical Rev.*, **31**, 691, 1928.

⁷⁶ Rice and Byck, *P.R.S.*, **50**, 132, 1931.

THE USE OF THERMIONICS IN THE STUDY OF ADSORPTION OF VAPOURS AND GASES.

BY JOSEPH A. BECKER (*Bell Telephone Laboratories, New York*).

Received 3rd December, 1931.

The object of this paper is to point out a relatively new but very powerful tool in the study of adsorption phenomena. This tool is thermionic emission. While it is not applicable to all surfaces and all kinds of adsorbents, it makes up for these deficiencies by the insight it gives us into the nature of adsorption processes. The results obtained thus far from this tool have come largely as by-products of the study of thermionic emission of electrons. When the primary emphasis is placed upon the study of adsorption itself, one can confidently expect an abundant yield. This is quite apparent when one surveys the results obtained thus far.

These results apply when strongly electropositive metals such as caesium, barium, or thorium or strongly electro-negative gases such as oxygen are adsorbed on surfaces of metals such as tungsten, molybdenum, or platinum. In these cases: the adsorbed particles exist either as adions (adsorbed ions) or adatoms; the ratio of adions to adatoms decreases as the surface concentration increases; the rate of evaporation of adions or of adatoms varies rapidly—perhaps exponentially—with the surface concentration; as the concentration of adions plus adatoms increases the rate of evaporation of adions decreases while that for adatoms increases; the heat of adsorption or the energy required to remove an individual atom from the surface depends upon the concentration of similar adatoms and is greatly affected by the presence of other kinds of adatoms; the mean adsorption time or mean life of an adsorbed particle is a function not only of the temperature but also of the concentration; particles adsorbed in a given region of the surface behave like a two-dimensional gas and migrate to other regions—there is some indication that this may happen only above some critical temperature analogous to the melting-point in solids.

The key to these results is the fact that the thermionic electron emission from tungsten and similar metals varies by very large factors and in a characteristic manner when small amounts of electropositive metals are adsorbed on the surface. Fig. 1 illustrates this fact for caesium, barium, and thorium on tungsten at 1100° K. It shows the logarithm of the emission current in amperes per cm^2 vs. f , the fraction of the surface covered. The three curves are quite similar to one another. They differ chiefly in the height at the maximum or so-called "optimum." This optimum occurs when the tungsten is covered with a single layer of adsorbed particles.¹ When the surface is covered with two or three layers, the emission current has the value characteristic of the adsorbed material in bulk. For any value of f greater than zero, the current with caesium is greater than that with barium, and this in turn is greater than

¹ *Physical Rev.*, **28**, 341-361, 1926.

that with thorium. Between $f = 0$ and $f = 0.8$, the shape of each curve is such that its slope at any f is proportional to $(\log i_1 - \log i_f)$ where the subscripts refer to the value of f . The ratio of the current at the optimum to the current from clean tungsten, *i.e.* $\frac{i_1}{i_0}$ depends on the temperature; as the temperature decreases, this ratio increases. Thus,

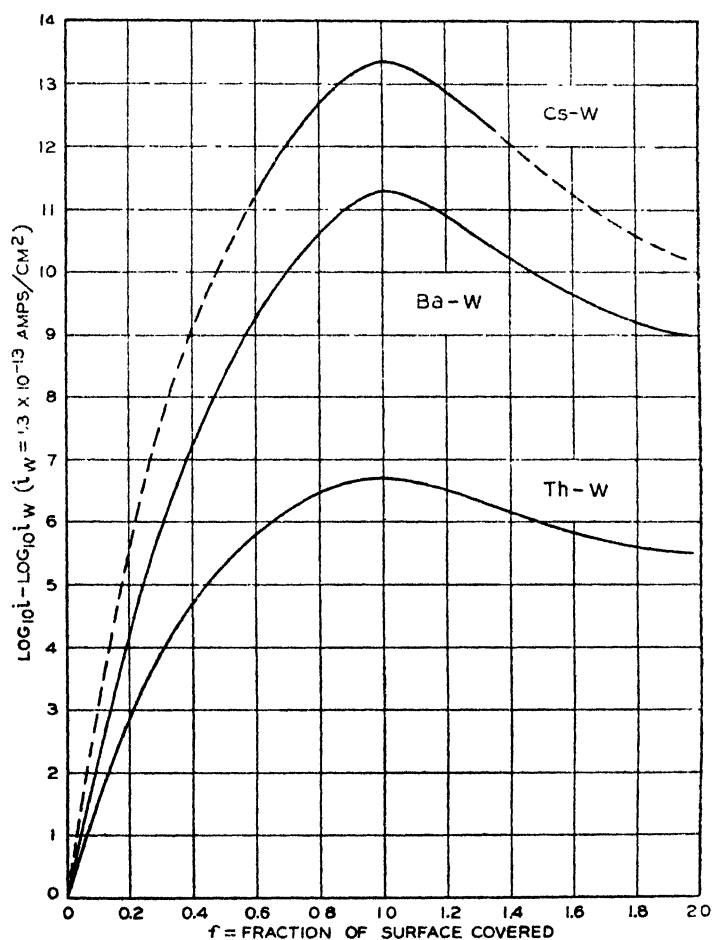


FIG. 1.

for caesium on tungsten $\log \frac{i_1}{i_0} = 13.3$ at 1100°K. while it is approximately 19 at 800°K.

The similarity in the general shape of these curves is all the more striking since they can be obtained in three distinct ways, depending upon the method by which the material is deposited on the tungsten surface. In the case of caesium, the tungsten is exposed to caesium vapour. Caesium atoms arrive at the tungsten surface at a rate determined by the vapour pressure which in turn is usually determined by the temperature of bulk caesium in the tube. The barium is deposited on the tungsten

by flashing a primary barium-alloy filament at a fixed temperature for a fixed time.² Each flash deposits a small but definite amount of barium on the tungsten. Thorium can be deposited in this second way. It can also be made to arrive at the tungsten surface by diffusion from the interior of thoriated tungsten³ along the grain boundaries,⁴ by glowing the tungsten at an activating temperature for various lengths of time. These three methods may be designated as the vapour, evaporation, and diffusion methods. The details of the use of these methods are fully described in the original articles, to which references are given.

From the $\log i$ vs. f curves of Fig. 1, it is possible to determine how the "work function" of the surface varies with f . While the exact definition of the work function is quite complex, it will be sufficient for the purposes at hand to think of it as the work an electron must do to escape from the metal surface. It is customarily expressed in equivalent volts, *i.e.* the potential difference in volts through which an electron would have to fall from rest in order to be able to do this amount of work. This work function W in volts is obtained by solving Richardson's Equation in its logarithmic form,

$$\log i = \log A + 2 \log T - W \frac{e}{2.3kT} \quad (1)$$

For our purposes A may be treated as a universal constant whose value is 60 amps./cm.²°K². If W is expressed in volts and T in °K, $\frac{e}{k}$ is numerically equal to 11,600. From Fig. 1 and equation (1) we can determine W for any value of f .

Fig. 2 is a plot of this relationship for caesium, barium, and thorium on tungsten for $T = 1100$ °K. The work function for tungsten is very materially reduced when its surface is more or less covered with electro-positive materials. The effectiveness of the adsorbed material, in reducing W is large at first, but decreases more and more until the surface is covered with a complete layer. Additional layers increase W until at two or three layers, W approaches the value characteristic of the adsorbed material in bulk. A careful study of the curves reveals that the minimum value of W is approximately equal to the resonance potential of the adsorbed particles in vapour form; and that $\frac{dW}{df}$ is proportional to $(W - R)$ from $f = 0$ to $f = 0.8$, where R is again approximately equal to the resonance potential or the minimum value of W .

In the attempt to explain these facts, we can learn a good deal about the nature of the adsorbed particles. It might at first sight appear that the enhanced emission of Fig. 1 is to be ascribed to electrons emitted from the adsorbed particles. While this may be true for f larger than about 2, it cannot be true for the first layer. If it were true, the excess current above that from clean tungsten should be directly proportional to f and should increase steadily to the value characteristic of the adsorbed material. Instead of this, experiment shows that $\log i$, rather than i , increases linearly with f for small values of f , and that the emission passes through a pronounced maximum.

Another hypothesis which is capable of explaining these as well as

² *Physical Rev.*, **34**, 1323-1351, 1929.

³ Langmuir, *Physical Rev.*, **22**, 357-398, 1923.

⁴ Clausing, *Physica*, **7**, 193, 1927.

other observed facts is the so-called "adion grid theory"⁵ An adion is defined as an adsorbed particle whose valence electron no longer rotates about its own nucleus but has been absorbed by the underlying metal. This definition is similar to that for an ion in a compound such as caesium chloride. That both adions and adatoms may exist on one and the same surface at the same time was shown in a previous paper.⁶ Of course, any particular particle may be an adatom at one instant and an adion at a later instant and vice versa.

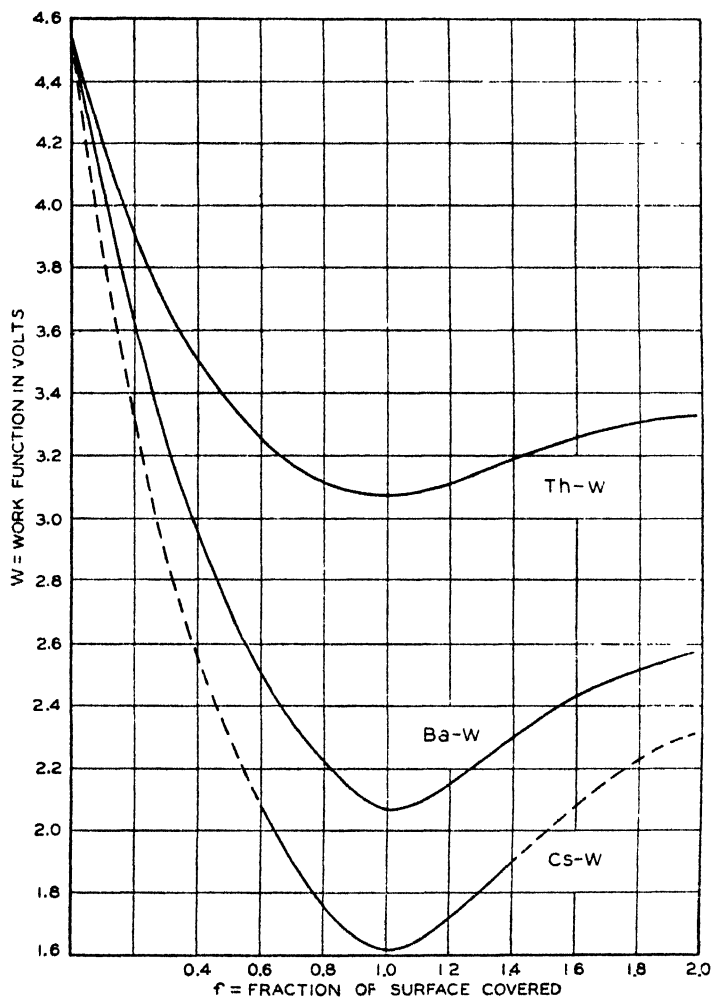


FIG. 2.

These adions act like a positively charged open meshed grid placed very close to the tungsten surface. Such a grid and its negative image produce zero field at some distance beyond the grid and an average field of $4\pi\sigma = 4\pi eN_p$ between it and the tungsten, provided that the size of the grid is very large compared to its distance from the surface.

⁵ *Trans. Am. Electrochem. Soc.*, **55**, 153-175, 1929.

σ is the charge on the grid per cm.^2 of surface. N_p is the number of positive ions per cm.^2 . If l is the radius of the adion in cm. , then the potential difference between any point in the metal and the point outside at some distance from the surface is $4\pi e N_p l$. This means that the work an electron must do to escape has been reduced by $300 \cdot 4\pi \cdot 4.77 \cdot 10^{-10} N_p \cdot l$ volts. Hence

$$\Delta W = W_0 - W = 1.80 \cdot 10^{-6} N_p l \quad (2)$$

This equation can be used to determine values of N_p . For any particular f , ΔW can be read off from Fig. 2. The radius of the adion, l , can be found in tables obtained from X-ray data⁶ or tables based on quantum theory calculations.⁷ The only unknown is N_p .

It is then possible to determine P , the percentage of adsorbed particles that are adions, since

$$P = \frac{N_2}{N} \quad (3)$$

where N is the total number of adsorbed particles. N is very simply related to f , since

$$f = \frac{N}{N_1} \quad (4)$$

where N_1 is the value of N for $f = 1$. An approximate value of N_1 can be computed from the known or estimated values of atomic diameters, d , and the type of surface packing. From simple geometrical considerations, it follows that for loose packing

$$N_1 = \frac{1}{d^2} \quad (5a)$$

while for close packing

$$N_1 = \frac{2}{(\sqrt{3} d^2)} = \frac{1.15}{d^2} \quad (5b)$$

Since close packing appears more probable than loose packing, the calculations that are to follow will be based on close packing. It should also be realised that in the derivation of equations (5a) and (5b) it is assumed that the number of particles in the monatomic layer is not affected by the size and arrangement of the underlying atoms. This may not be true, or it may be true only if the size of the adions is larger than the atomic size of the base metal, or it may be true only at low temperatures. In any event, it will be a rather simple process to recompute the data when more reliable values of N_1 are available for barium and thorium. For caesium, the value of N_1 has been obtained by direct observation.

Table I gives the values of P , the percentage of adsorbed particles that are ions, for various values of f . The values of l and d , used in computing P , are also given. In some cases, the values of l have been obtained by interpolation.

It is also desirable to know how the tendency to form adions varies as f increases. As a measure of this tendency, we may take $\frac{dN_2}{dN}$, which represents the ratio of the increment in the number of adions to a small

⁶ Goldschmidt, *Trans. Faraday Soc.*, **25**, 253-283, 1929.

⁷ Pauling, *Jour. Am. Chem. Soc.*, **49**, 765, 1927.

TABLE I.

l = radius of singly charged ion. d = diameter of neutral atom.
 N_1 = number per cm.² when $f = 1$. f = fraction of surface covered.

	$l \times 10^8$.	$d \times 10^8$.	$N_1 \times 10^{-14}$.	Per Cent. Ions: (P).					
				$f = 0.1$.	0.2.	0.4.	0.6.	0.8.	1.0.
Cs	1.65	5.2	4.2	55	48	40	33	28	23
Ba	1.6	4.4	5.9	28	27	23	20	17	14
Th	1.6	3.5	9.4	13	12	9.5	7.9	6.6	5.4

increment in the total number of adsorbed particles. From equations (2) and (4) and the experimental fact that

$$\frac{dW}{df} = -aN_1(W - R) \quad (6)$$

where a is constant; it follows that

$$\frac{dN_p}{dN} = \frac{a}{1.8 \times 10^{-6}}(W - R) \quad (7)$$

This means that the tendency to form adions is directly proportional to the amount by which the work function of the surface exceeds the resonance potential of the adsorbed particles. The proportionality constant depends upon the nature of the adsorbed particles.

On the basis of the adion grid theory, it is easy to see why the tendency to form adions must decrease as f or N increases. For as N increases, N_p will increase. As a result, the adsorption field, which helps electrons away from the surface, increases. Consequently, more electrons leave the underlying metal to neutralise the adions, and fewer electrons leave the adatoms and enter the underlying metal.

Evaporation of Positive Ions and of Atoms.

The adsorption fields greatly affect the rate of evaporation of positive ions. Since these fields are in a direction to help electrons out of the surface, they should make it more difficult for positive ions to escape. Experiments with caesium on tungsten¹ fully confirm this prediction. In fact, they show that in a region from $f = 0.01$ to 0.20 , the more caesium there is on the surface, the less evaporates in any given time, and any caesium that does evaporate comes off as ions. For very small values of f , the ion evaporation rate increases with the concentration. It comes to a maximum when the surface is only about 1 per cent. covered. These experiments show that the forces on an adion, due to neighbouring adsorbed ions and atoms, are appreciable even when the average separation is 10 atom diameters.

At first sight, one might expect E_a , the rate of evaporation of neutral atoms to be unaffected by the adsorption fields and consequently directly proportional to f . But this is not the case. Actually, the evaporation rate at a given temperature increases rapidly with the surface concentration. As a first approximation, E_a increases exponentially with f . Such evaporation curves for caesium on oxidised tungsten at various temperatures were given in a previous publication.⁵ For caesium, barium,

thorium and oxygen on tungsten, similar curves, though not so accurate nor so complete, have been obtained.

The interpretation to be put on these curves is that while the adatom as a whole is neutral, the forces on the various parts of the atom are not zero. This is undoubtedly due to the fact that the adsorption fields vary so rapidly with the distance from the surface. In these fields, the net force on an atom is much the same as on a negatively charged particle, since the atom evaporation curves are similar to the electron evaporation curves.

The technique employed to obtain such evaporation curves depends upon the adsorbed material. For caesium on tungsten,¹ the evaporation rate E at a given temperature T and a given f , is equal to the arrival rate whenever equilibrium prevails. The arrival rate can readily be obtained from the saturation positive ion emission.¹ f is obtained by suddenly decreasing the temperature of the surface to a sufficiently low value and noting the time that elapses before the electron emission reaches its optimum value. During this time, every atom that strikes the surface sticks to it. At the optimum emission, the surface is covered with a monatomic layer. The observed time, multiplied by the arrival rate, gives the number of atoms that were added before a monatomic layer was reached. The difference between this number and N_1 , the number corresponding to a monatomic layer, gives the number N which were present at the prevailing T and arrival rate. In this way, a single point on an E vs. f curve is obtained. To get other points, the process is repeated for other surface temperatures and for other arrival rates.

For barium² or thorium³ on tungsten, the process is as follows: A definite amount of barium or thorium is deposited on the tungsten. The electron emission from this surface is then determined at a testing temperature so low that the amount on the surface is not thereby altered. From a log i vs. f curve similar to Fig. 1, f is obtained. The surface is then heated for a short time to a temperature at which evaporation takes place. The emission is determined at the testing temperature. From this, a new value of f is obtained. The decrease in f , divided by the time in seconds and multiplied by N_1 , gives E in atoms per cm.² per second for the mean value of f . If this process is continued, E can be determined for other values of f , and a complete E vs. f curve obtained. The whole process is then repeated at another temperature at which evaporation takes place.

These evaporation curves allow us to draw conclusions as to the way in which the "heat of adsorption" or work necessary to remove an individual atom or ion depends upon the concentration. If this heat or work did not depend upon f , then the rate of evaporation should be directly proportional to f . Since the rate decreases with increasing f for ions, but increases more rapidly than proportional to f for atoms, we conclude that as the surface concentration increases, the heat of adsorption increases for ions, but decreases for atoms.

If a complete family of accurate E vs. f curves at various values of T were available, numerical values of the heat of adsorption could be obtained for various values of f from the slope of a plot of $\log E$ vs. $\frac{1}{T}$.

Another interesting quantity that can readily be obtained from a family of E vs. f curves is τ , the mean life of an adatom, or the average

¹ See also Andrews, *Physical Rev.*, **33**, 454, 1929.

number of seconds an atom spends on the surface under various conditions. It can be shown that τ is very simply related to E and f , namely that

$$\tau = N_1 \frac{f}{E} = f t_1. \quad (8)$$

t_1 is the time required to deposit one layer if every atom sticks and the arrival rate is equal to E .

Table II., taken from a paper on "The Life History of Adsorbed Atoms and Ions," gives values of τ for various values of f and T . The large values of τ are rather surprising. This table also emphasises the dependence of τ on f as well as on T .

TABLE II.—MEAN LENGTH OF LIFE OF CAESIUM ATOMS.
On a Tungsten Surface Partially Covered with Oxygen (Cs on OW)
 $N_1 = 4.0 \times 10^{14}$ atoms/sq. cm.

Fraction of Surface Covered: f .	Temperature ° K.	Time to Form One Layer: t_1 sec.	Mean Life, τ sec.
0.8	700	830	665
0.8	725	133	106
0.8	740	60	48
0.8	760	22	18
0.80	700	830	665
0.85	700	350	300
0.90	700	135	121
0.95	700	59	56
1.00	700	28	28
0.2	910	133	27
0.4	840	133	53
0.6	780	133	79
0.8	725	133	106
1.0	675	133	133
1.2	625	133	160

Surface Migration.

The thermionic emission characteristics are useful in studying surface migration. This technique apparently is well adapted for a quantitative investigation of the factors involved in the movement of adsorbed atoms. Briefly this technique is exemplified by depositing barium on one side only of a flat tungsten ribbon. The thermionic current emitted from each side of the ribbon is measured under standard testing conditions and is used to determine the amount of barium on each side. The ribbon is then flashed at a temperature

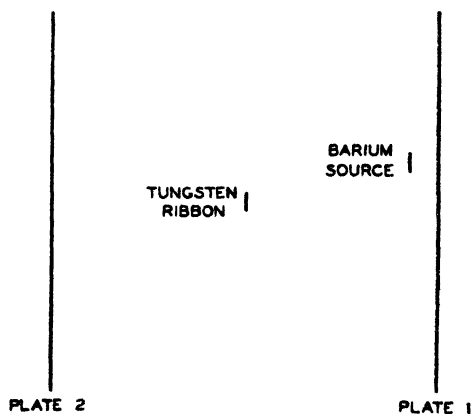


FIG. 3.

between 900° K. and 1100° K. for a short period of time. The emissions are redetermined under standard testing conditions. This flashing and testing is repeated until the emissions from both sides are not altered by flashing.

Fig. 3 is a simplified diagram of the tube used, while Fig. 4 is an idealised curve of the result. The first part of Fig. 4 shows how the logarithm of the current from the front side (i_1) and from the back side (i_2) changes as barium is deposited on the front side of the tungsten ribbon. The deposition is discontinued when $f = 0.80$ on one side. Subsidiary tests show that during this deposition and testing no barium reaches the back side of the ribbon. For the second part of Fig. 4, the tungsten ribbon is flashed at about 1000° K. Periodically the flashing is interrupted, while i_1 and i_2 are determined under the standard testing conditions. As a result of this flashing, the emission from the front side decreases rapidly at first and then more and more slowly; while the

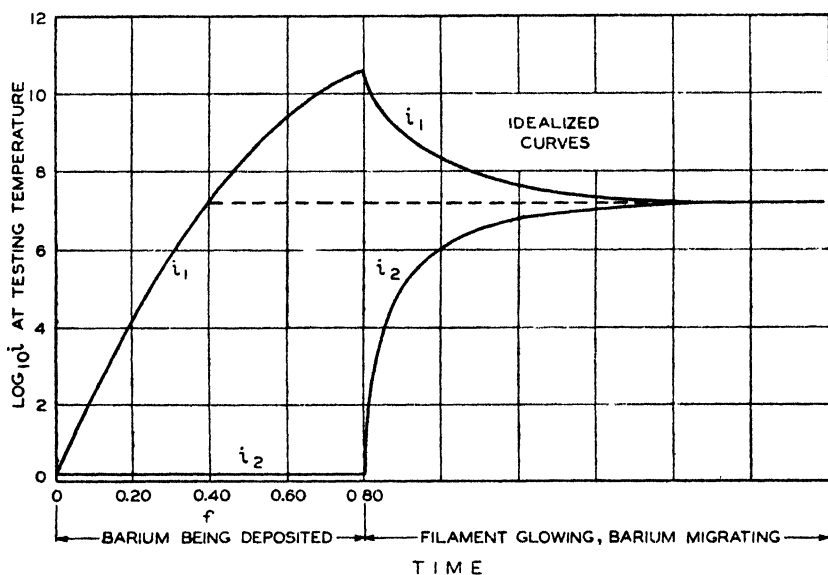


FIG. 4.

emission from the back side increases very rapidly at first and then more and more slowly. When the total time of flashing has continued for one or two hours, the emissions from the front and back sides are equal and do not change appreciably with further flashing. The value of this emission corresponds to $f = 0.40$ whereas originally f for the front side was 0.80 and for the back side was 0.00. Furthermore at any stage of the flashing the sum of the f values for the front and back sides is 0.80. In other words, the material that was originally on the front side redistributes itself until it is uniform; the back side gains what the front side loses.

In actual practice, the current observed on plate 1 is nearly equal to i_1 ; but the current to plate 2 consists not only of i_2 but also of electrons which come from plate 1 as a result of reflection or secondary emission. The result of this is that the measured current to plate 2 is never less than 1 per cent. of the current to plate 1. When i_2 is much

smaller than i_1 this is serious, but as i_2 approaches i_1 the errors become negligible. Furthermore the difficulty can be greatly lessened by inserting appropriate shields in the tube. Very likely if the currents were measured by means of a properly designed Faraday cage arrangement, it could be eliminated entirely.

Diffusion.

Still another application of thermionics to surface phenomena is in the study of diffusion from the surface into the interior and vice versa. An example of this is the diffusion of thorium to the surface of thoriated tungsten.⁴ Another example is the diffusion of barium and oxygen in the case of oxide coated filaments.² As far as they go these studies suggest the following picture: There is a certain amount of work involved when an atom is transferred from the interior of a body to its surface. This work depends upon the surface concentration; it may also depend upon the temperature. For each volume concentration there exists a surface concentration in equilibrium with it. If the surface concentration is much less than the equilibrium amount, every atom that reaches the surface stays there. If the surface concentration exceeds the equilibrium value, its rate of decrease is rapid at first but decreases more and more until equilibrium is established.

Oxygen on Tungsten.

While most of the results described relate to electropositive materials, similar results appear probable for electronegative substances such as

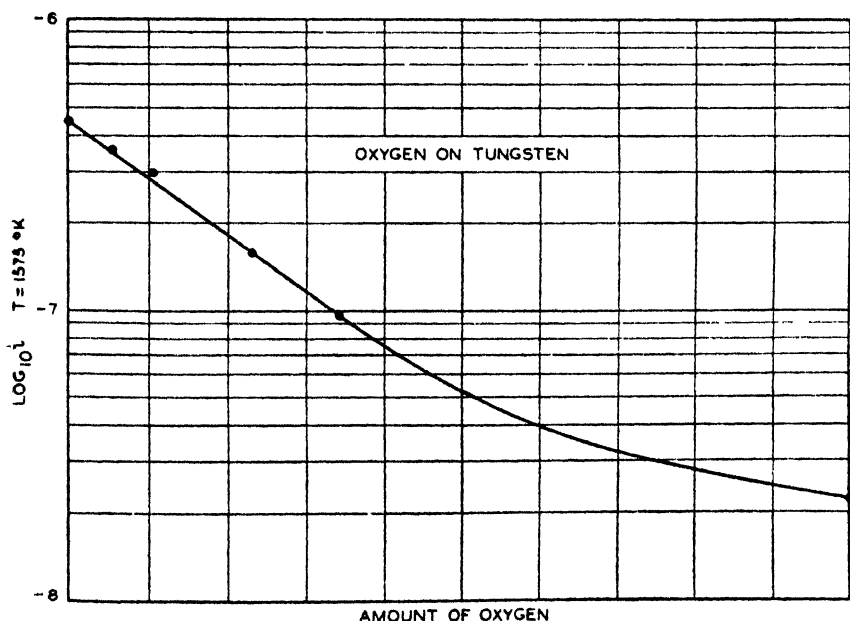


FIG. 5.

oxygen. Fig. 5 shows how the logarithm of the emission from tungsten varies with the concentration of adsorbed oxygen. The absolute value

of the amount of oxygen is not known. One might venture to guess that the maximum amount in this figure corresponds to half a layer. From the fact that the emission decreases it follows that oxygen forms negative adions. Since the magnitude of the slope decreases as f increases, the tendency to form adions decreases as the oxygen concentration increases.

Experiment shows ² that the rate of evaporation of adsorbed oxygen increases very rapidly with the surface concentration. Hence the heat of adsorption must decrease as the concentration increases. Other experiments show that oxygen migrates very rapidly at 1400° K.

Summary.

Thermionic emission can be very useful in the study of adsorption phenomena. The primary reason is that very minute amounts of electro-positive elements, such as caesium, barium, or thorium, or electronegative gases, such as oxygen, change the thermionic emission from surfaces of tungsten, platinum, molybdenum, etc., by very large factors and in a characteristic manner. They do this by changing the work function of the surface. This effect, as well as other surface effects, can be best explained by the adion grid theory: The adsorbed particles can exist on the surface either as adions (adsorbed ions) or as adatoms; the adions act like a positively charged, open meshed grid placed very close to the surface. From this theory and the experimental facts it follows: (1) That the ratio of adions to adatoms decreases as the surface concentration increases (Table I.); (2) that the work required to remove an adion from the surface increases while the work to remove an adatom decreases as the surface concentration increases; (3) the mean life of an adsorbed particle depends on the surface concentration as well as on the temperature (Table II.); (4) the rate of diffusion from the surface into the interior depends upon the temperature and on the amount by which the surface concentration exceeds its equilibrium value. Thermionic experiments show the existence of surface migration and can be used to make a quantitative study of this phenomenon. The techniques involved in these various experiments are described and references given to previous publications.

ADSORPTION OF SATURATED VAPOURS BY POROUS SUBSTANCES. EXPERIMENTAL METHODS.

BY F. G. TRYHORN AND W. F. WYATT.

Received 8th December, 1931

The comparatively few adsorption measurements in which values have been obtained for the amounts of two components adsorbed from a solution or a mixture led the authors to develop simple methods for studying the adsorption by porous substances of saturated vapours under conditions in which the composition as well as the amount of the adsorbate could be determined. Most of the methods described have been previously recorded in these *Transactions*, and are therefore presented in summary form for the purposes of the present discussion.

I. Adsorption of a Saturated Vapour.

(a) In early experiments a rather tedious procedure was adopted in which a weighed quantity of activated coconut charcoal or silica gel was suspended in a small pan by a fine platinum wire from the left arm of a balance beam so that it swung freely over the surface of a pure liquid of which the vapour was to be adsorbed. The liquid was contained in a jacketted vessel maintained at constant temperature by circulation of water from a thermostat: this vessel stood on a bridge placed across the balance pan, and its top was closed by a wooden cover carrying a glass tube drawn out to a fine aperture through which passed the suspension wire. The process of adsorption was followed by counterpoising the suspended adsorbent by weights on the right balance pan at frequent intervals until saturation occurred.

With liquids of low vapour pressure saturation required several days. Measurements were made by this method of the adsorption of the vapours of pure liquids by charcoal and gave concordant evidence of the two stages in the adsorption, *viz.* adsorption of vapour *qua* vapour, followed by the sudden formation of a liquid surface on the charcoal through condensation of the adsorbed vapour.

(b) The labour involved in the above method was great and to lessen it an automatic recording balance was devised. In this device the suspended pan of adsorbent was hydrostatically counterpoised by a short metal rod, hung from the right arm of the balance beam and partly immersed in a liquid of high density and low vapour pressure. The liquid was kept at constant temperature in a jacketted glass vessel through which water at 25° was pumped. By this arrangement, as the weight of the adsorbent increased the balance beam moved through a series of equilibrium positions, raising the metal rod progressively from the immersion liquid: the movement of the balance beam caused a corresponding movement of a small concave mirror of stainless steel, mounted on a rocking lever, one end of which was attached to the right end of the beam by a fine hooked platinum wire. Movements of this mirror were recorded by the reflexion of a spot of light on to a piece of bromide paper carried on a rotating drum which was driven electromagnetically. The proportions of the lever and the distance of the drum from the mirror were so calculated that the vertical displacement of the end of the balance beam over its maximum range of travel (0.6 cm.) corresponded with a movement of 14 cm. of the spot of light on the bromide paper.

The liquid used was a paraffin oil fraction, b.p. 250-260°, density 0.8352 at 20°: in conjunction with a rod of 3.18 mm. radius this gave a range for the balance of 0.1592 gm.: by using β -bromo-naphthalene (d.₄ 1.605) as immersion liquid and a rod 1.0 cm. radius the range could be increased to 3.026 gm. Separate light sources, flashing at variable periods, were focussed on the drum to give time signals to calibrate the weight record in measuring adsorption velocity.

The electromagnetic drive to the drum was controlled by an electric seconds pendulum which drove a clock mechanism in which variable contacts on the minute wheel completed the drum circuit at 2, 15, 30 or 60 sec. intervals, causing the drum to rotate in 1.25, 9.375, 18.75 or 37.5 hours respectively. The balance was calibrated before and after an experiment by the addition of weights to the balance pans: when the balance had come into equilibrium after the addition of a weight the lamp focussed on to the mirror was flashed momentarily to record a

spot on the drum which corresponded with the weight in question. After adsorption was complete the second calibration was made in a similar manner by adding weights to the right balance pan to bring back to beam to its initial position. After the record had been developed the calibration and time marks enabled it to be scaled off in both time and weight units.¹

A balance of this type gives very satisfactory service and by building up the rotating drum on a broken gramophone motor, and using a simply constructed electric clock² the cost of conversion of a normal balance to an automatic one was kept down to £2 10s.

II. Adsorption from Binary Saturated Vapours.

(a) If from a mixture containing A_0 and B_0 grams of two components X and Y respectively, the amounts a and b are adsorbed, the final concentration of X in the mixture will be $100 (A_0 - a)/(A_0 + B_0 - a - b) = A_F$. Thus if we can measure the total weight adsorbed, x , and also the final concentration of X , we can calculate the values of a and b from the equations $a + b = x$, and $(100 - A_F)A_0 - A_F(B_0 - x) = 100a$. The most rapid and accurate method of analysis of binary mixtures of pure liquids is by refractometric examination, the accuracy increasing with the difference in the refractive index of the two liquids.

The H_α line, and 20° were taken as reference standards throughout the work, and refractive index curves for the various pairs of liquids were constructed from measurements of mixtures carefully made up by weight.

In making an adsorption measurement by this method a gram of activated adsorbent was placed in a flat-bottomed $6'' \times 1''$ glass tube, and a small test-tube (about $\frac{1}{2}'' \times 1\frac{1}{4}''$), with a short leg about $\frac{5}{8}''$ long sealed on to the bottom, was dropped into the larger tube: the latter was then drawn out in the blowpipe flame to a narrow tube about $2''$ from the top. After cooling and weighing, 2 or 3 c.c. of a given binary liquid mixture was run into the small test tube by means of a capillary pipette: the tube was then sealed off at the constriction and both parts weighed together. The tube was placed in a thermostat, and after a definite time interval was dried, opened, and the refractive index of the residual liquid determined, and the increase in weight of the charcoal measured. For a given pair of liquids about 20 such tubes were prepared, and were opened at times ranging from 1 hour to five days. From these measurements it was possible to construct curves showing the composition of the adsorbate as functions of total adsorbate or of time, by means of the above equations.

(b) **Vapour Composition Curves.**—Since the experiments measured primarily the adsorption from the vapour phase it was essential to know the composition of the vapour in equilibrium with the liquid mixtures of known composition. As no values were recorded in the literature for the systems examined the necessary data were obtained by a separate series of experiments, by a method based on the equations given above. A weighed amount of a mixture of known composition was placed in a long-necked bulb of about 10 c.c. capacity which was connected through an expansion vessel to a manometer, pump, and constant pressure device. The bulb and expansion vessel were submerged in a thermostat

¹ Tryhorn and Wyatt, *Trans. Faraday Soc.*, **21**, 399, 1925; **22**, 139, 1926; **23**, 238, 1927; **24**, 1, 1928.

² *Electric Clocks*, Messrs. Cassell & Co., Ltd.

at 20°. The liquid in the bulb was shaken in the earlier experiments, but in later ones stirred by an electromagnetic stirrer, while the pressure in the apparatus was slowly lowered until slow boiling commenced: this was continued until about 0.1 to 0.15 gm. of the mixture had evaporated: the loss of weight and the composition of the residue were then accurately determined. By substituting these values in the above equations the weights of each component in the vapour phase were found, and from this the weight percentage composition of the vapour in equilibrium with the liquid in the bulb.

III. Determination of the Pore Volume of the Adsorbents.

Several methods were used in measuring the pore volumes of the charcoal and silica gel utilised in this work. These methods gave results which were in agreement, but were all based on the assumption that the molecular volume of the adsorbed liquid is the same as that of the bulk liquid: on this ground the values found are open to criticism, but the consistency of results obtained with liquids of very different compressibility renders it probable that, except perhaps for those molecules actually in contact with the surface of the adsorbent, the bulk molecular volume does apply to the adsorbate.

(a) The first derivatives of the curves obtained when the weight of vapour of a pure liquid adsorbed per unit weight of adsorbent was plotted against time showed sudden breaks which were identified with the moments at which the pores were filled and a liquid film formed on the surface of the adsorbent. From the amount of vapour adsorbed at these points, assuming that the molecular volume is the same as in bulk, pore volumes of reasonable consistency (0.16 to 0.18 c.c. per gram of adsorbent) were obtained.

(b) A check on the above value was obtained by soaking charcoal in a liquid until saturation was ensured, and then determining the loss in weight as a function of time: the volume of liquid present when the liquid film just disappeared from the surface was taken as the pore volume. These two methods gave results which fell close together, those from the second method being slightly lower than those from the former.

(c) The relative accuracy of the above methods was checked in the case of silica gel by determining the differential heats of wetting of the gel when various amounts of liquid were present in it. Samples of the gel were prepared containing known percentages of a liquid such as acetone: the heats of wetting of these specimens by acetone were then measured, and the heats of wetting per gram of gel plotted against the acetone contents. Extrapolation of such curves to zero heats of wetting was made, the intercept on the acetone-content axis being taken as the pore volume of the gel. The values so obtained were found to be the mean of those obtained by the above methods.

PRESSURE MEASUREMENTS FOR INVESTIGATING THE MUTUAL BEHAVIOUR OF ADSORBED HYDROGEN ATOMS.

By M. C. JOHNSON, M.A., D.Sc.

Physics Department, Birmingham University.

Received 23rd December, 1931.

1. Introduction.—The present note is concerned with the cohesion of an adsorbed layer, or mutual attraction and repulsion between its constituent particles, rather than with their adhesion to the adsorbent. There are many important cases in which adhesion to individual atoms of the solid is small enough not to be the main factor in controlling the lateral extension or aggregation of the adsorbed layer. There is well-known experimental evidence from electron scattering and from condensation of molecular rays that such cohesion can range from lattice-like to fluid-like behaviour of an adsorbate.

The state of aggregation of adsorbed atomic hydrogen is of particular interest, since in this case the intermolecular forces cannot be deduced from knowledge of cohesion in any pure phase; we are dealing with a substance which can only maintain stable existence in the adsorbed condition, the atoms being recombined into molecules in the gaseous, liquid and solid phases. We proceed to assess some of the conditions under which it becomes possible to study H_1 atoms remaining in proximity to each other without forming H_2 . The first need is for quantitative data as to closeness of this proximity in a layer adsorbed at the gas-solid interface.

2. Density of Packing of Atoms in Layer.—If hydrogen in a perfectly sealed enclosure at constant temperature is known to be undergoing partial dissociation by some agency confined to the gaseous phase, measurements of its fall of pressure may yield information as to the structure of an adsorbed layer, on the very probable general hypothesis that atoms can remain on surfaces they strike much longer than can molecules. For quantitative accuracy the following conditions must be fulfilled:—

(a) The initial stage when no atoms exist on the surfaces exposed, and the final stage when surface density of atoms has reached its maximum for given conditions of the gaseous phase (stage of "saturation," but not necessarily close packing), must both be precisely determinable. For this it is necessary to ensure a complete tracing of the various "fatigue" phenomena affecting rate of pressure fall.

(b) It is necessary to choose an adsorbent which is not itself likely to dissociate molecules at its surface, as for instance may occur with Tungsten and Oxygen. Vitreous surfaces are preferable to metals in this particular; for at many metallic surfaces dissociation of the gas may have to be regarded as a consequence of, not a cause of, adsorption, in which case an atomic layer might have begun to form immediately on exposure to any stray H_2 , thus making impossible the fulfilment of (a).

(c) No other solids beside the given adsorbing surface must make any contribution to loss or gain from the gaseous phase.

(b) and (c) can be satisfied only if metals are completely eliminated from the adsorption vessel. This was not possible in the pioneer measurements of Langmuir on atomic hydrogen, since the hot filaments used as dissociating agent themselves contribute to gas losses, by processes such as those investigated later by Dillon.¹

For this reason I investigated pressure losses in adsorbable hydrogen, devising continuous-reading methods of elucidating the factors in "fatigue" to comply with (a), and avoiding all metal surfaces for the sake of (b) and (c) by using as dissociating agents (i) electrodeless induced discharges, and (ii) the impact of mercury vapour atoms after their excitation by $\lambda 2537$.²

The further assumptions then needed for determination of the packing of atoms in the adsorbed layer are:—

(d) Loss of N molecules from a given volume of the gaseous phase implies gain of 2N atoms to the adsorbed phase over a given area. This is based on the assumptions, valid for many practical conditions, that adsorption of normal H_2 is negligible compared with that of H_1 , that excited H_2' (which is not necessarily as slow to adsorb as normal H_2) is not the principal product of the disturbances (i) or (ii) proceeding in the gas, and that the temperature is not low enough for condensation of H_2 which possibly occurs under liquid air conditions.

(e) Magnitude of the given area of adsorbing solid is equal to the geometrically measurable area. This assumption is the weakest and is certainly invalid, in the strict sense, for all surfaces except those just solidified; but if fresh glass or silica walls are thoroughly baked, but not acid treated or bombarded, this unavoidable error is probably less than for microcrystalline metals whose surface has suffered oxidation, etc. The error may reach, under optimum conditions, the order of 50 per cent.; and this accessible surface may itself be not so much vitreous as covered with the gases which diffuse continuously out of the best baked vitreous materials.

Subject to the error (e), the methods described in the papers enable initial and final stages in saturation to yield a sequence of pressure measurements fulfilling (d); these gave, under varied conditions, the following order of variation in measured maximum packing of H_1 atoms in the adsorbed layer, incidentally confirming monomolecular thickness and atomic state of the adsorbate:—

(i) 5.9×10^{15} , 5.3×10^{15} , 3.2×10^{15} per $cm.^2$, using electrodeless discharge.

(ii) 1.2×10^{15} , 1.0×10^{15} per $cm.^2$, using photosensitised dissociation.

The experimental conditions of (i) must have included molecules and atoms in various states of excitation and ionisation in the gaseous phase, and it is only the degree of packing which makes it unlikely that the layer contains much else beside neutral H_1 . The experimental conditions of (ii) can include no ions and no excited H_1' but only normal neutral atoms, and possibly the bye-product HgH , which itself may possibly be adsorbable. In comparing the packings, it must be remembered that forces of attraction and repulsion between excited H_1' are probably different from those between normal H_1 ,³ and hence layers formed under

¹ T. J. Dillon, *Proc. Physical Soc.*, **41**, 546, 1929.

² M. C. Johnson, *Proc. Roy. Soc.*, **123**, 603, 1929; **128**, 447, 1930; *Proc. Physical Soc.*, **42**, 490, 1930.

³ Kemble and Zener, *Physic. Rev.*, **33**, 512, 1929; Eisenschitz and London, *Z. Physik*, **60**, 523, 1930.

conditions (i) and (ii) would exhibit (if fluid-like), different two-dimensional pressures, and (if lattice-like), different spacings.

3. Conditions under which Adsorbed H_1 can Recombine and Desorb as H_2 .—A necessary (and until lately considered sufficient) condition that an H_1 atom encountering another H_1 shall form the desorbable H_2 , is that a third body shall be present to receive the surplus energy in the formation of the stable molecule. This third body may be a gas molecule or a "catalytic" surface. Atoms packed to the above measured surface densities must be continually within "collision" distance unless they constitute a very rigid lattice. The adsorbed layer of H_1 would accordingly be expected to be in a constant state of desorption by pairing of its constituents, and only capable of being maintained by a constant supply of freshly adsorbing atoms from the gaseous phase. It is possible that such a non-static maintenance of layer plays considerable part in electrode phenomena at the liquid-solid interface, but at the gas-solid interface under the above conditions this is not the case: for the pressure curves of all the above experiments show no rise at room temperature, following a removal of either of the types of dissociating agent used, partial desorption only setting in at 200° – 300° C. This continued stable existence of a sheet of non-combining atoms might be explained by saying that their valency is saturated by the adsorption itself, were it not that they recombine readily enough with fresh atoms striking them from the gaseous phase. This has been investigated by many workers beside the present author, by means of the heating of the surface during attack by fresh atoms of however small kinetic energy.

Accordingly the experiments enforce a conception of H_1 atoms at mean distances of mutual separation only slightly exceeding the diameter of their normal Bohr orbits, and yet in mutual repulsion from each other, while still capable of attraction by and combination with similar H_1 impinging from the gaseous phase.

4. Cohesion Between Atoms in the Layer.—The above facts might be taken as pointing to a perfect gas state of the adsorbed atomic hydrogen, if it were not that the further investigation yielded some indirect qualitative evidence of cohesion between neighbouring adsorbed atoms; this is distinct both from their common adhesion to the solid surface, and from the mutual repulsion which gives them such rigid preference for gas atoms instead of adsorbed neighbours in the far stronger attraction needed for recombination. By analysing the curves of pressure fall into terms representing condensation, spontaneous desorption, and desorption due to recombination with atoms from the gas, the last of these three processes was found to be variable, and to depend on the packing density in the layer; ⁴ this was only explainable if, when a gas atom strikes an adsorbed atom, the latter's neighbours can exhibit a tendency to restrain the recombination from taking place. The work done in releasing an adsorbed atom cannot, therefore, be solely against the attraction of the solid, but is also against a slight cohesion with other adsorbed atoms.

Adding such data to the previous, it becomes necessary to regard the adsorbed atoms as exhibiting both (a) a mutual repulsion preventing molecule formation among themselves, and, superposed on this, (b) a slight mutual attraction giving an incipient tendency to a state of aggregation whose packing would be loose (due to the repulsion), compared with the closeness of atoms within a single molecule.

⁴ M. C. Johnson, *Proc. Roy. Soc.*, **132**, 67, 1931.

That is, the adsorbed layer possesses both of the characteristics of a (very) imperfect gas below its critical state and tending to condense into a lattice of wide spacing.

In classical theory no such combination of properties could rationally be ascribed to H_1 , though of course H_2 molecules exhibit mutual attraction in very slight degree.

The quantum mechanical treatment of intermolecular forces alone explains the existence of H_1 atoms mutually repelling at distances such as found in the above experiments: the most recent development of this to include van der Waals' forces accounts also for the slight superposed attraction. It is possible that such treatment of combined attraction and repulsion nowadays considered possible to non-combining H atoms in certain states will evaluate a theoretical structure of this adsorbed layer, to which the above experiments may possibly provide, in certain features, a rough demonstration.

ON MIXTURE ISOTHERMS AT ACTIVE POINTS.

BY H. DOHSE AND H. MARK.*

Received 11th December, 1931.

In a paper¹ dealing with the catalytic decomposition of isopropyl alcohol into water and propylene on bauxite it was possible to recognise that in the case of this reaction the water serves to retard the reaction so long as it remains in contiguity with the active centres of the catalyst. If the water is continuously removed as it is formed a reaction of zero order results. From this it may be concluded that in this case the active spots of the contact material are surrounded by *alcohol* molecules, provided only that there is present in the gas space a measurable alcohol pressure. This can be established by adsorption experiments. In the case of the retarded reaction also the active places are all surrounded, either with alcohol or with water. The proportion of active spots surrounded by alcohol to those surrounded by water, depends on the partial pressures of the two gases in the gas space, for the retardation of the decomposition increases strongly with rise in the concentration of water vapour. On the other hand, however, the distribution on the active places must also depend on temperature since the retarded reaction is more strongly dependent on temperature than the unretarded one. The difference in the heat of activation amounts to about 13,000 cal. It was shown in the above-mentioned paper that this figure is identical with the heat of adsorption of water on the same bauxite, as was demonstrated by Dr. Schuster, although it was not possible to give a theoretical explanation of the fact. This explanation has not up to the present been forthcoming and will indeed remain wanting, until by means of the isotherms of mixtures we have a sufficient knowledge of the zone of saturation. Let us assume that in such a case the heat of activation of the hindered reaction decreases, as well as that of the true heat of activation, as the difference between the heats of adsorption of

* I. G. Farbenindustrie A-G., Ludwigshafen a/Rh.

¹ Dohse and Kälberer, *Z. physik. Chem.*, **5B**, 131, 1929.

the inhibited and of the reacting materials. This, however, presupposes that, in regard to saturation in the case of adsorption of a mixture, the distribution of the two adsorbates on the adsorbent is determined solely

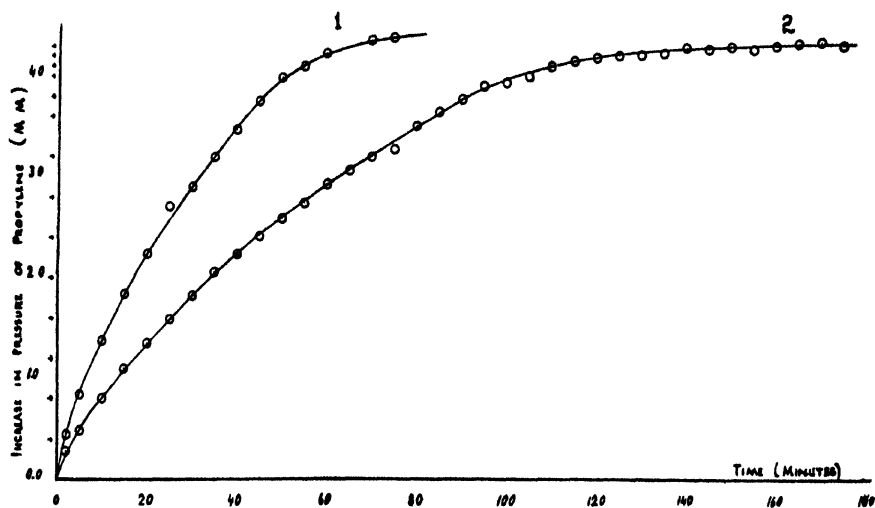


FIG. 1.—The course of the decomposition of Isopropyl Alcohol on Baucite.

Curve 1 End pressure $p_E = 4.45$ Temperature $t = 183^\circ$.

Curve 2 " " " $= 4.32$ " $t = 176^\circ$.

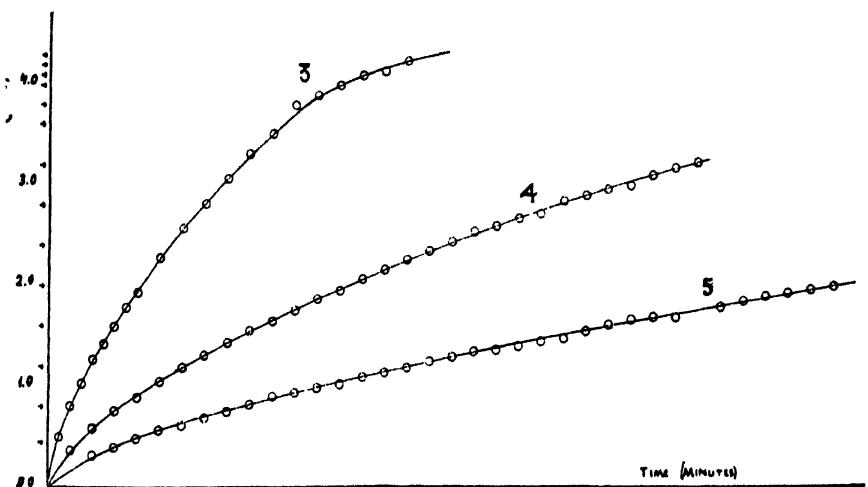


FIG. 2.—Decomposition of Isopropyl Alcohol on Baucite.

Curve 3 $p_E = 4.33$ $t = 167$

" 4 4.36 156

" 5 4.36 145.5

by the power e of their heats of adsorption, without regard to the volumes of the respective phases. Taylor is of this opinion, and accordingly he postulates that the heat of desorption, arising from the heat balance on the contact substance, is not identical with the measured heat of

adsorption, although the difference between activated and inactivated adsorption cannot be distinguished by means of calorimetric measurement. The experiments about to be recorded gain in interest by reason of this theory of Taylor. We shall show that by the aid of this catalytic

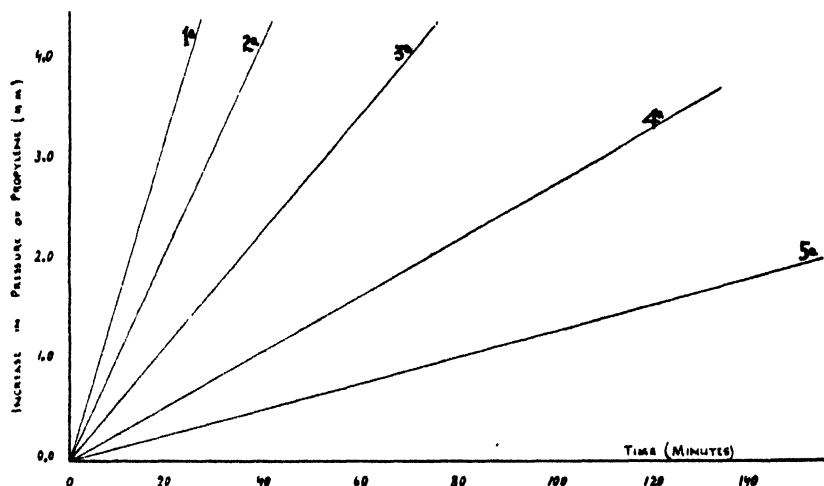
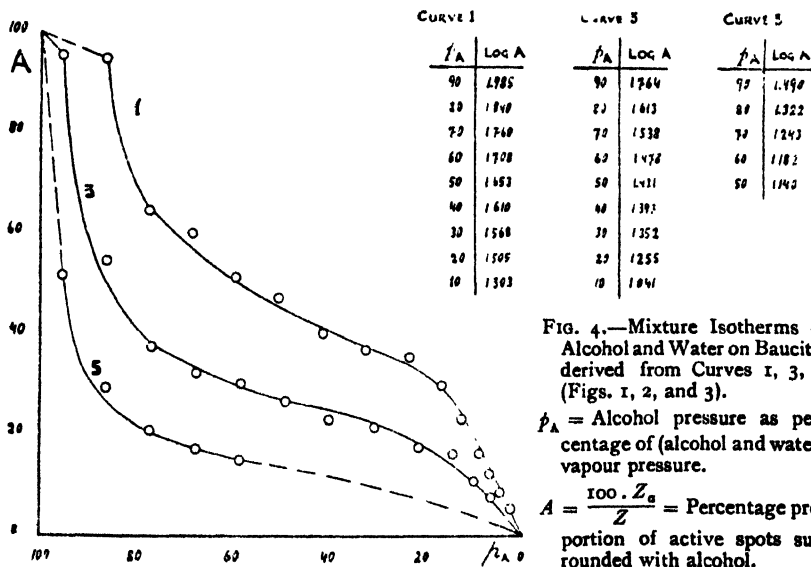


FIG. 3.—The course of the decomposition of Isopropyl Alcohol in Baucite when the water formed is continuously removed.



method of measurement we render available a satisfactory means of determining the isotherms of mixtures on active spots.

If the number of active spots be z , and those which are surrounded by alcohol and by water respectively are z_a and z_w , then—

$$z_a + z_w = z \quad . \quad . \quad . \quad . \quad (1)$$

The reaction constant on the active spots which are surrounded by alcohol, k , must naturally be equally great at the same temperature for the retarded and for the unretarded reaction. The velocity of the reaction is v and in the case of the hindered reaction v' . The true heat

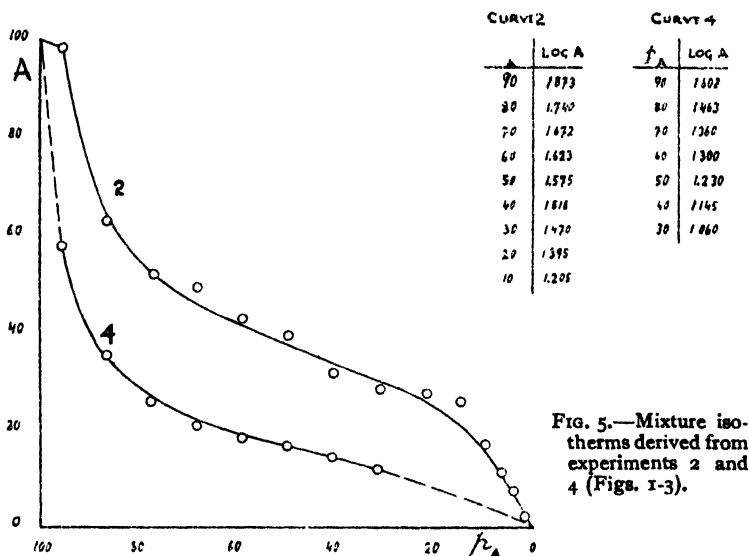


FIG. 5.—Mixture isotherms derived from experiments 2 and 4 (Figs. 1-3).

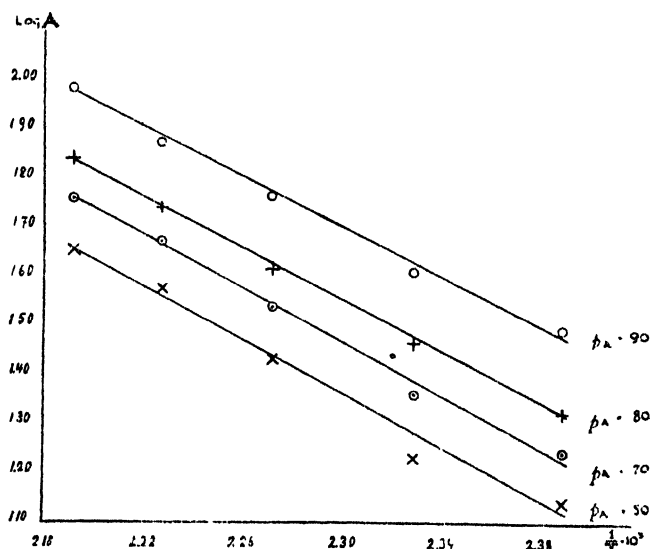


FIG. 6.—Temperature relationship of the alcohol layer at constant partial pressure of alcohol (p_A) derived from experiments 1 to 5.

of activation is q and the heat of reaction of the hindered reaction is $q + b$. We obtain thus at constant temperature—

$$\begin{aligned}
 v &= z \cdot k \\
 v' &= (z - z_w) \cdot k. \\
 \frac{v'}{v} &= \frac{z - z_w}{z} = \frac{z_a}{z}.
 \end{aligned}$$

The relationship between the velocity of reaction in the retarded and in unretarded conditions furnishes us thus in every respect, according to definition, with the fraction of the active spots which are surrounded by alcohol. If we plot this against the percentage proportions of alcohol and water in the gas space, we have the mixture isotherm for a given total pressure of alcohol plus water. We derive this percentage proportion also from the reaction velocity curves, since one water molecule corresponds to each alcohol molecule decomposed and the sum of the two remains constant. Figures 1 to 3 show the measurements for the retarded and the unretarded reaction. The percentage distribution in the gas space and the percentage distribution in the contact mass (according to the above scheme) was calculated for the pressures which are marked with an arrow. Figures 4 and 5 show these two values in relationship with one another. We see that these mixture isotherms are curves with characteristic bends, concerning which we cannot at present give an explanation. If we plot the logarithms of the values of the distribution derived from these curves, against the reciprocal of the temperature, at a given constant pressure of alcohol and water, we get straight lines, as is shown in Fig. 6. The heat effect corresponding to the slope of these lines amounts to about 12,000-13,000 calories = b .

Summary.

It is shown that with the assistance of the catalytic decomposition we can derive good mixture isotherms at active points, if it is possible to measure the retarded and the unretarded reactions.

ON THE BEHAVIOUR OF ADSORBED ATOMS.

BY J. CHARITON, N. SEMENOFF AND A. SCHALNIKOFF (*Physico Technical Institute, Leningrad, U.S.S.R.*).

Received 30th November, 1931.

When a surface of a solid is exposed to the vapours of another substance, a rarified film of adsorbed molecules is formed at first. This film must have—and, as it was shown by the experiments of Volmer and Adhikari¹ on "creeping" of molecules of benzophenone, it apparently has—the properties of a two-dimensional gas. If the temperature of the surface is lower than the temperature of the vapours we shall obtain finally a deposit of condensed substance which will gradually grow.

It was pointed out by M. Knudsen² and R. W. Wood³ that the formation of this deposit cannot take place if the temperature of the surface is not low enough. It was shown later by N. Semenoff and J. Chariton⁴ that this "critical temperature of condensation" depends on the density of vapour acting on the surface, and from the figures obtained by them J. Frenkel⁵ (who first gave the theory of the phenomenon), calculated the latent heat of evaporation of a cadmium "doublet"—two cadmium atoms

¹ *Z. physik. Chem.*, **119**, 46, 1926.

² *Phil. Mag.*, **30**, 300, 1915; **32**, 364, 1916.

⁴ *Z. Physik*, **25**, 287, 1924.

³ *Ann. Physik*, **50**, 472, 1916.

⁵ *Ibid.*, **26**, 117, 1924.

linked together. Later I. Estermann⁶ and J. Cockroft⁷ have done more accurate measurements for various substances. N. Semenov⁸ then proposed a very simple scheme of the phenomena, considering the equilibrium between three-dimensional vapour, two-dimensional vapour, and two-dimensional condensed phase. Semenov's point of view is that the critical temperature for the given density of three-dimensional vapour corresponds to the point where the two dimensional "condensation" may take place. If the temperature of the surface is increased the density of two-dimensional gas must also be increased in order to be saturated, and this can be done by increasing the density of three-dimensional vapour. Thus at the critical temperature corresponding to a definite pressure of vapours (or at the critical pressure corresponding to a definite temperature)—shortly speaking, at the critical conditions—we have an equilibrium three-dimensional vapour—two-dimensional vapour—two-dimensional condensed phase.

The density of two-dimensional vapour is proportional (unless it is too large) to the pressure of three-dimensional vapour. Therefore from the critical temperature critical density curve (which shows at the same time how the pressure of two-dimensional vapour depends on temperature) it is possible to calculate the latent heat of two-dimensional evaporation. The slope of the curve mentioned must be smaller than the slope of the curve showing the normal three-dimensional pressure against temperature. Therefore, the two curves must intersect at some point corresponding to a certain temperature. At this temperature the surface need not be overcooled with respect to the substance in order that the deposit may appear. The theory of Semenov predicts some discontinuities in the adsorption isothermal above the critical point. The remarkable results of experiments on adsorption of gases published by A. J. Allmand and L. C. Burrage⁹ are, maybe, an example of such phenomena.

Some experiments have been done in order to find the above-mentioned point of intersection, *i.e.* to trace the curve in the region of higher temperatures than it, has been done before. In connection with these experiments it was necessary to use a method of registration of critical conditions which would give results certain enough. The method similar to that of I. Estermann was used, but more attention was paid to the factor of time. The deposit was formed on glass, or on a layer of naphthalene or sulphur previously condensed on glass from vapours. The temperature of the glass was kept constant by means of drops of liquid air, which was poured into the mercury filling the glass tube. The density of the stream of molecules falling on the glass (or any other substance) was determined by the temperature of the oven from which cadmium or mercury was evaporated. This temperature was measured by means of a thermocouple.

The results obtained¹⁰ are very different from those published by Estermann. As a matter of fact it was possible to obtain a curve similar to that of Estermann, but only in cases when the time of the experiments was restricted to several minutes only, *i.e.* to the time necessary for an amount of substance sufficient to form a visible deposit to reach the surface. If, however, at a given density, we increase the tem-

⁶ *Z. physik. Chem.*, B. 7, 471, 1930.

⁸ *Proc. Roy. Soc.*, 119, 293, 1928.

⁷ *Z. Elektroch.*, 31, 441, 1925.

⁹ *Ibid.*, 130, 610, 1931.

¹⁰ The experiments were carried out by O. Leypunsky, M. Lebedinsky and M. Gen. A detailed account will be published elsewhere.

perature of the surface above the "critical" value, the deposit will appear if we wait long enough. One might think that above the "critical" temperature the condensation (which must take place finally because the surface is over-cooled in respect to the vapour) proceeds by means of a mechanism substantially different, so that the critical temperature might remain, but an analysis of the results obtained leaves no room for this conception.

In Fig. 1 the time of formation of a visible deposit of cadmium is plotted against the temperature of the surface of the glass covered with naphthalene. The density of the molecular beam (calculated from

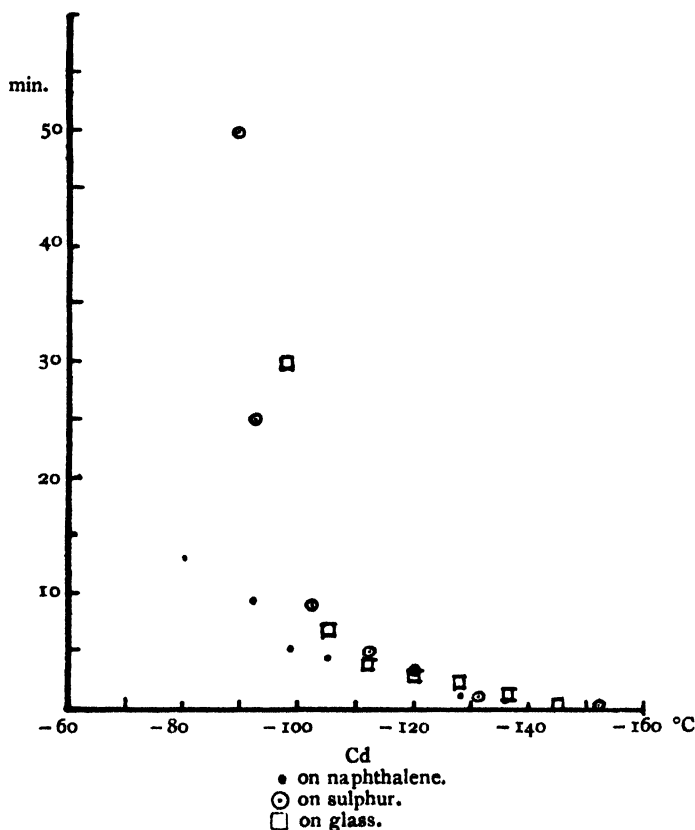


FIG. 1.

the temperature of the substance and the dimensions of the apparatus) is equal to $2 \cdot 10^{14}$ molecules per cm^2 per second. It is obvious that the curve does not give anything like critical temperature, but just that the time of formation is gradually rising as the temperature increases.

Quite similar results have been obtained with cadmium deposited on pure glass-surface or on glass covered with a layer of sulphur and with mercury deposited on copper. The experimental results for cadmium on glass and sulphur are also shown on Fig. 1. Fig. 2 shows the curves obtained with mercury.

This absence of critical temperature seems to contradict the theory of Semenov. However, the discrepancy disappears if we take into

account the inhomogeneity of the surface. Various points of the surface correspond to various heats of adsorption. At a certain temperature condensation may take place on the most active points, and then spread around these centres gradually covering the whole surface. At a lower temperature the condensation may begin on all points of the surface and the deposit becomes visible in a much shorter time. This supposition is supported by the fact that the deposit obtained at a higher temperature—corresponding to long time exposure—has not a smooth metallic appearance, but seems dark and very irregular in density, while a deposit obtained at a temperature 30° lower has a typical mirror-surface. The existence of points of various activity seems to be a fact well estab-

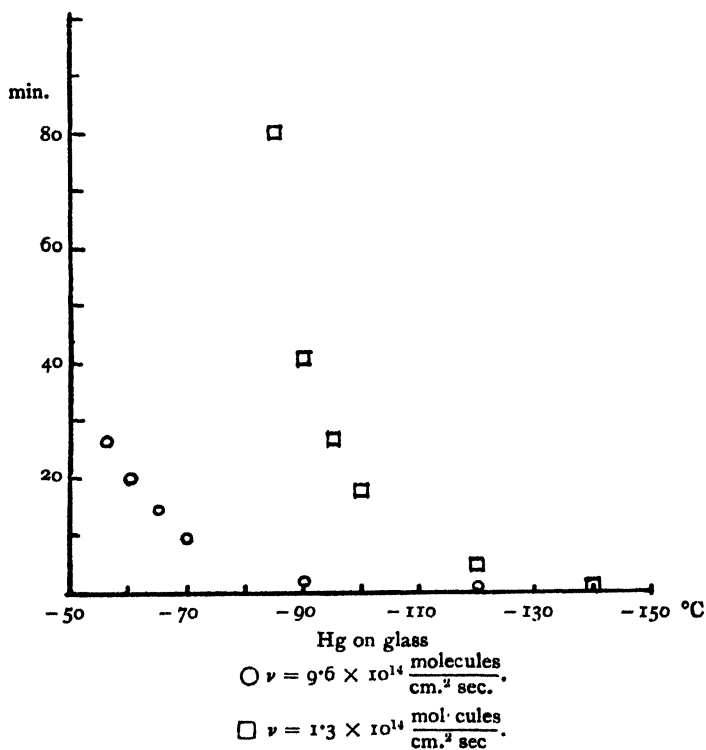


FIG. 2.

lished by the work of Taylor, and it is quite reasonable to take into account these results when considering the mechanism of condensation. In this case the theory of critical temperature of condensation proposed by Semenoff explains the experimental results quite satisfactorily.

In this theory, as well as in many other cases, the conception of a two-dimensional gas is used. It must be noticed that in the case considered this conception is not absolutely necessary. It is possible to consider the equilibrium between singlets and doublets or larger complexes from a purely energetical point of view, taking into account only the exchanges produced by condensation from the volume and evaporation from the surface into the volume. It will be shown¹¹

¹¹ See page 176.

that the equilibrium is obtained more quickly through the "two-dimensional" collisions. Regard must also be had to the fact that the existence of the atoms bombarding the surface makes it possible to produce the centres of condensation in a quite peculiar way. For example several atoms can group themselves together into two layers and the evaporation of such a complex will be much more difficult than the evaporation of a complex consisting of the same number of atoms, but lying in one layer.

We shall reproduce now the results of some very simple calculations by one of us (J. Chariton) concerning the behaviour of rarified adsorbed layer.

There is a great difference in the character of the motion of molecules of an ordinary three-dimensional gas and those of a two-dimensional gas formed on the surface of a solid. For the molecules of ordinary gas the mean free path is determined only by the density of the gas. It is quite obvious that this does not hold for "two-dimensional" molecules. The fact of formation of deposits geometrically limited by the slits forming molecular beams shows that the molecules stay near enough to the place where they fall. If the molecules could move freely along the surface colliding only one with another a molecular beam of density, say 10^{13} molecules per cm^2 per second could not give any image at all.

From experiments of Clausing¹² we know that the time of the life of an atom on the surface of the adsorbent is less than 10^{-6} second. Let it be even 10^{-8} second, then the number of molecules per cm^2 of the surface n shall be

$$n = \nu \tau = 10^{13} \times 10^{-6} = 10^7$$

The mean free path corresponding to this n may be calculated from the formula.¹³

$$R = \frac{1}{2 \, d n} \approx \frac{1}{2 \cdot 2 \cdot 10^{-8} \cdot 10^7} = 2.5 \text{ cm.},$$

where d is the diameter of the adsorbed atoms. Thus the atoms of the beam striking the surface might distribute over a large surface and we could not get anything like a sharp-defined image of the slit.

On the other hand the movement of the molecules along the surface of a solid certainly exists. This has been shown extraordinarily clearly by the experiments of Volmer and Adhikari.¹ Other indirect experiments also give evidence of the creeping of the molecules.¹⁴

Let us consider the character of the movement of an atom remaining on the surface. It is quite clear that even on an ideal surface of a crystal different points must possess different properties. For example an atom adsorbed just "above" one of the ions of the lattice must certainly have a somewhat different potential energy from that of an atom placed "between" two ions. The surface is, in an energetic sense, "wavy." Therefore an atom possessing a certain amount of vibrational energy cannot leave a point of minimum potential energy unless the energy of its vibration is sufficient to reach the heights of surrounding maximums. If the maximum is reached the adsorbed atom may pass to the next minimum, where it will stay for some time, etc.

¹² *Over den Verblyfsted van Moleculen en de strooming van zeer verdunde Gassen*, 51, Amsterdam, 1928.

¹³ Referring only to the order of magnitude.

¹⁴ I. Estermann, *Z. Physik*, 33, 320, 1925. *Z. physik. Chem.*, 106, 403, 1923. M. Volmer und I. Estermann, *Z. Physik*, 7, 1, 13, 1921.

The distance from one minimum to another must be of the order of inter-atomic distances in a solid, *i.e.* several units multiplied by 10^{-8} cm. The movement of the adsorbed atoms should consist of jumps of, say $3 \cdot 10^{-8}$ cm. distributed chaotically in all directions. Thus we can apply to our case the well-known formulæ of brownian movement and write

$$\frac{\delta}{t} = \frac{\Delta^2}{\tau_0} = 2D \quad . \quad . \quad . \quad (1)$$

where δ is an average displacement in a certain direction of an adsorbed atom during the time t , Δ is the elementary displacement, *i.e.* the distance between two minimums of potential energy, τ_0 the time corresponding to each replacement, and D the diffusion coefficient of two-dimensional gas. Let ω be the frequency of vibrations of adsorbed atoms, then the probable value of a displacement occurring during one second will be

$$\omega e^{-\frac{h}{RT}} \quad . \quad . \quad . \quad (2)$$

where h is the "height" of the maximum in relation to the minimum. Then

$$\tau_0 = \frac{1}{\omega e^{-\frac{h}{RT}}} = \frac{1}{\omega} e^{\frac{h}{RT}} \quad . \quad . \quad . \quad (3)$$

from 1 and 3 we obtain :

$$h = RT \log \omega \tau_0 = RT \log \frac{\omega \Delta^2}{2D} \quad . \quad . \quad . \quad (4)$$

As the order of magnitude of ω and Δ is known we need only the diffusion coefficient in order to get a rough estimate of h .

We can obtain the value of D if we utilise some results of other authors. For example D can be calculated from Volmer and Adhikari's¹ experiments on the creeping of benzophenone, on a glass surface. We can write

$$G = Ds \frac{dn}{dt} t,$$

where G is the amount of transported benzophenone, s —the length of the line over which the molecules are creeping, $\frac{dn}{dt}$ —the gradient of density of molecules on the surface, and t —the time of experiment. One of Volmer's experiments gives :

$$\begin{aligned} G &= 22 \times 10^{-7} \text{ gr.}, \\ s &= 0.05 \text{ cm.}, \\ \frac{dn}{dt} &= 5 \times 10^{-6} \frac{\text{gr}}{\text{cm.}^3}, \\ t &= 2.5 \text{ hours.}, \end{aligned}$$

whence we get

$$D \cong 5 \times 10^{-4},$$

and

$$h = RT \log \frac{\omega \Delta^2}{2D} \cong RT$$

and

$$\tau_0 \cong \frac{1}{\omega}.$$

This is certainly too small a value,¹⁵ because it gives for real velocity v of the molecule $\frac{\Delta}{\tau_0}$ a value bigger than the corresponding value obtained from the formula,

$$v = \sqrt{\frac{3RT}{\mu}}$$

which cannot take place. This strange result may depend on the fact that our calculations may not be applicable to such a large complex as a benzophenone-molecule, which probably covers at once many minima and maxima points of the surface, and might therefore have Δ corresponding to several inter-atomic distances.

Another estimate might be done on the basis of the experiment of Cilliers described in Stern's article on molecular rays in *Ergebnisse der exacten Naturwissenschaften*, Vol. III.¹⁶ A deposit of antimony was obtained by means of a diaphragm having its width unequal along its length. The deposit was formed much more readily under wide parts of the diaphragm than under the narrow central part. It is stated that the intensity of the beam was constant over all the image. The difficulty of formation of the image in the narrow parts ($< 10^{-2}$ cm.) is explained on the assumption that in these parts the equilibrium is shifted because the adsorbed atoms may creep away from the exposed surface, while in the wide parts only the atoms on the very edge of the image will not be replaced by newcomers. As the equilibrium between three-dimensional and two-dimensional gas is reached in the time of the order τ , we must allow for the atoms of antimony to creep over 10^{-2} cm. during the time τ (if they should creep more slowly the equilibrium would not be appreciably shifted. Thus

$$\frac{10^{-4}}{\tau} = \frac{\Delta^2}{\tau_0}.$$

$$\text{or} \quad \tau_0 = \frac{\Delta^2}{10^{-4}} \tau \approx \frac{10^{-15}}{10^{-4}} \tau = 10^{-11} \tau.$$

The absence of data for τ makes it impossible to get a numerical value for τ_0 .

Another experiment of similar kind has been published by I. Estermann,¹⁷ who worked with cadmium. In this case we might use the value of τ estimated by Clausius, i.e. $\tau \approx 10^{-6}$ sec. But here we come again to an absurd result, since τ_0 becomes 10^{-17} sec. (the dimensions of the deposit were of the same order as in the experiment of Cilliers, so that we can use the same formula). This again leads us to the assumption that the elementary displacement is not of the order of interatomic distances. Let the elementary displacement be λ , then the time corresponding to it will be $\frac{\lambda}{v}$, where v is the velocity of the adsorbed atom.

$$\text{Then} \quad \frac{10^{-4}}{\tau} = \frac{\lambda}{\left(\frac{\lambda}{v}\right)^2} = \lambda v,$$

or

$$\lambda = \frac{10^{-4}}{\tau \cdot v} \approx \frac{10^{-4}}{10^{-6} \sqrt{\frac{3RT}{\mu}}} \approx \frac{10^{-4}}{10^{-6} \sqrt{\frac{3 \times 8.31 \times 10^7 \times 180}{112}}} \approx 5 \times 10^{-3} \text{ cm.}$$

¹⁵ ω is of the order $\sim 10^{12} \sim 10^{13}$, let it be 3×10^{12} . Δ is of the order $3 \cdot 10^{-8}$.

¹⁶ The original dissertation could not be obtained.

¹⁷ *Z. Physik*, 33, 320, 1925.

In this case (as well as in the case of benzophenone) λ should probably be treated in the light of Frenkel's¹⁸ conception. Anyway, this high mobility is rather surprising; it might be due to the fact that in the experiments cited one never deals with a really clean surface. The impurities might make the surface energetically smooth. However this explanation does not seem to be entirely satisfactory.

The results of some experiments, as yet unpublished, suitable for calculation of τ_0 and h were kindly given to me from the laboratory of Electro-Vacuum Works "Swetlana" in Leningrad. The experiments dealt with creeping of thorium along the surface of tungsten. The velocity of creeping at temperatures about 2000° K. was estimated to be about 1 micron per minute. This corresponds to the value of h about 100,000 cal./mol. if the elementary displacements is put equal to 3×10^{-8} cm. The value of the same order was obtained for h from the measurements of the thermal coefficient of diffusion of thorium to the surface of a tungsten wire, and it has been shown previously that this diffusion takes place along the surfaces of the micro-crystals forming the wire. It is interesting to notice that in this case where the surface is probably really clean we obtain reasonable results with Δ equal to interatomic distance.

The experiments cited, which were carried out for quite a different purpose, cannot indeed be taken as the confirmation of the expressed point of view on the movement of adsorbed molecules. A special experimental investigation is indeed absolutely necessary. It seems to us, however, quite unquestionable that the periodic structure of the surface must produce effects of the type described.

Let us consider now the problem, what kind of collision plays the more important part in the building-up of equilibrium in a two-dimensional layer formed by adsorption. There are collisions between adsorbed molecules and molecules of three-dimensional gas and purely two-dimensional collisions. The number of molecules per cm.² is $n = \nu\tau$. During one second the number of collisions of the first type will be $N_1 = \nu n \sigma = \nu^2 \tau \sigma$, where σ is the area of the molecule. The number of two-dimensional collisions per second will be $N_2 = \frac{n^2 \Delta d}{2\tau_0}$ (d being the diameter of the molecule) and the ratio

$$\frac{N_1}{N_2} = \frac{2\nu^2 \tau \sigma \tau_0}{n^2 \Delta d},$$

as however $d\Delta$ is (in the case of clean surface) of the order of σ and $n = \nu\tau$,

$$\frac{N_1}{N_2} \approx \frac{\tau_0}{\tau}.$$

Thus in equilibrium the number of "two-dimensional" collisions is as many times greater than the number of "mixed" collisions as τ_0 is greater than τ . As τ is in most cases less than 1 second and the equilibrium is reached practically in the same time it is obvious that, unless the density of two-dimensional gas is very large (and therefore not proportional to ν), mixed collisions should not play any important rôle in the considered processes on the surface.

¹⁸ *Z. Physik*, **59**, 640, 1930.

THE THICKNESS OF ADSORBED FILMS ON MERCURY.

BY H. CASSEL.

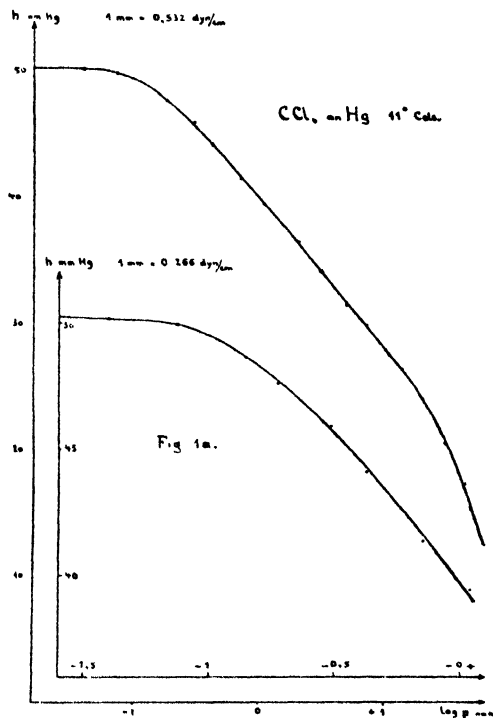
Received 7th December, 1931.

The application of the adsorption equation of Gibbs on the determination of surface densities of adsorbed substances has the advantage, over the mere observation of the adsorbed quantities, that it does not require a special measurement of the adsorbing surfaces. But the evaluation of the film thickness yet necessitates hypothetical suppositions on the range of the attracting forces and on the surface occupied by each molecule. The course of the adsorption isotherm, however, can give us important suggestions if the saturation of the first layer of molecules is well defined.

Generally the adsorption on aqueous solutions only shows the saturation of monomolecular films.¹ Recent results of F. Salditt² on the surface tension of mercury in an atmosphere of superheated benzene vapour also seemed to indicate the saturation of a second layer for the double value of surface density. Hence one gets a molecular area of about $3.2 \times 10^{-15} \text{ cm}^2$.

The interpretation of the step by step rise of the surface density as a layer by layer covering on the surface is not conclusive, because different orientations on the surface are possible if the size of

the molecules varies in different directions. Thus, it would be conceivable that the benzene rings which in a gaseous film lie flat on the mercury surface would displace each other and then stand on edge in a more condensed state.



FIGS. 1, 1A.

¹ N. K. Adam, *Physics and Chemistry of Surfaces*, Oxford Univ. Press, p. 29, 1930.

² H. Cassel and F. Salditt, *Z. physik. Chem.*, **155A**, 321, 1931.

An argument, however, against this possibility is the observed decrease of the adsorption heat of benzene with growing surface density.² The heat of adsorption falls from the rather high value of about 22,000

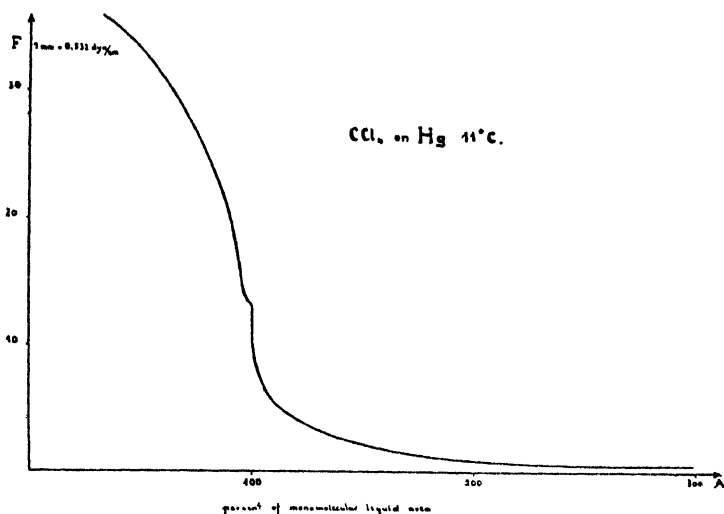


FIG. 2.

cal./mol. in the case of a nearly gaseous film to about 10,000 cal./mol. in the case of a more condensed film. This decay can only be explained by the greater distance of the later adsorbed molecules. The energy

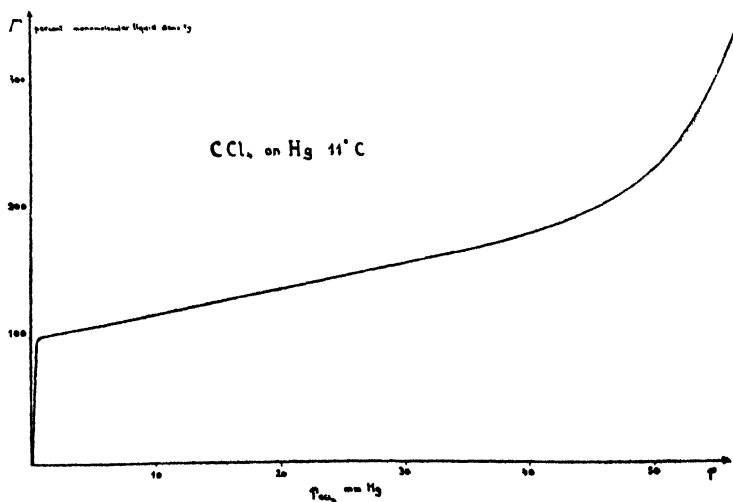


FIG. 3.

of adsorption of the first layer of benzene is evidently more than triple the heat of condensation. It is therefore somewhat doubtful whether

² H. Cassel, *Z. Elektrochem.*, **37**, 645, 1931.

the mutual erection of those benzene rings which lay flat can deliver sufficient energy to separate them partly from the underlying adsorbent.

The question for the thickness of the adsorption film can, of course, be answered with greater accuracy in the case of symmetrically formed molecules, *e.g.*, carbon tetrachloride where no packing effects are to be expected. For this reason, in co-operation with Mr. B. Gurevic I have studied the adsorption of CCl_4 by means of an improved apparatus with a higher degree of accuracy.

Fig. 1 shows the capillary curve at 11° Cels. plotted against $\log p$. Fig. 1a shows the range of the smallest vapour pressures on the double scale. In Fig. 2 a $(F - A)$ diagram is derived from the tangents of curve 1. Fig. 3 represents the adsorption isotherm. The two last curves indicate clearly a saturation at a surface density of $= 3.14 \times 10^{14}$ molecules per cm^2 . In order to determine the thickness of the film the area occupied by a CCl_4 molecule was computed from the density of the liquid at the adsorption temperature.

Saturation of the first layer is reached almost exactly when the surface density corresponds with that of a monomolecular film of liquid. It is remarkable that the adsorption above this point follows Henry's law over a considerable range. The density, continually rising, attains at the vapour pressure of CCl_4 in bulk a figure about 3.6 times that of the monomolecular film.

*Berlin-Dahlem,
Kaiser Wilhelm Institut für physikal Chemie.*

SORPTION OF GASES BY GLASS.

By F. P. BURT (*Manchester*).

Received 30th November, 1931.

The selection of glass as a material for the study of a solid-gas system is justified only by the fact that glass vessels are used in the majority of laboratory experiments with gases. When some physical constant of a gas is to be determined with great accuracy, a knowledge of the quantity of gas sorbed by the glass and of the pressure and temperature coefficients of sorption may be important. Thus a positive error may be introduced into a density determination if the traces of gas taken up by the walls of the density bulb are neglected.

The absolute quantities of gas taken up by the surfaces presented by ordinary gas apparatus are exceedingly small. A litre bulb, with a surface of some 480 sq. cm. would take up, at normal temperature and pressure, about 0.2 c.c. of ammonia, and a much smaller quantity of most other gases. When investigating the sorption phenomenon, therefore, it has been customary to use glass in the form of fine wool or powder, so as to secure a large surface.

Early experiments in Manchester indicated that approach towards equilibrium is extraordinarily slow, so that in addition to temperature and pressure a third variable, time, has to be taken into account.

An apparatus was designed which enabled the sorption process

to be followed at constant pressure. The glass sorbent in the form of fine wool or powder was packed into a tube which was connected through a differential pressure gauge with a second tube, immersed in melting ice and containing the gas under observation at the required pressure. This served as a pressure control. The sorption-tube was also connected with a vertical microburette expanding at its lower end into a bulb through which mercury could be admitted. The burette and its connections were charged with gas at the same time and to the same pressure as the control bulb. On admitting gas to the initially vacuous sorption tube the internal pressure was kept constant by regulating the inflow of mercury, and the quantity of mercury so introduced, after making due allowance for the dead-space of the sorption-tube, afforded a measure of the gas removed by sorption.

The usual preliminary treatment given to the glass was washing with alkali, chromic or nitric acid, and water, followed by drying in a stream of air. The final stages of drying were carried out *in situ* by repeatedly heating with and exhausting from dry ammonia at a temperature of 250° C. It was found that this treatment accelerates desiccation and leaves the glass in a condition that can be recovered after each sorption experiment by heating under exhaustion to a slightly lower temperature (200° C.). Complete removal of water is certainly not achieved, but the water content appears to remain unaltered provided that the glass is not exposed to temperatures higher than this.

It was found convenient to consider the isotherms by plotting the logarithms of the sorption values against the logarithms of time from the start of an experiment. The typical curve obtained in this way has the shape of a drawn-out "S" with a long, nearly linear middle portion which may have a gradient as steep as $\frac{1}{2}$, but the curve varies considerably with the condition and history of the glass and, in many cases, only portions of the "S" are observed. Sometimes the isotherm is almost linear over the whole experimental range: sometimes only a portion convex to the time axis is obtained: at other times only a concave portion. This last type of graph is found when the initial sorption is high.

For the system glass-ammonia data were obtained by Francis and the writer over a fairly wide range of temperature and pressure and, with the sample of glass wool used, it was found possible to express the fraction of sorption attained at any moment from the start of an experiment as a single-valued function of pressure, temperature and time.

The "S"-shaped log sorption, log time isotherms cannot be represented by any simple equation, but if $\log(\text{sorption rate})$, i.e. $\log\left(\frac{ds}{dt}\right)$, is substituted for $\log s$, graphs consisting of two linear portions united by a short curve are obtained (Fig. 1). For a series of isotherms at 0° C and under a number of different constant pressures, the first and second limbs of these rate graphs are parallel respectively: that is, the gradient is independent of the pressure. The isotherms cross each other, the highest pressure line starting at the top of the series and then bending over so that the second limb falls at the bottom.

In a series of experiments all at one and the same pressure but at different temperatures the rate graphs are precisely similar and the gradients of the linear portions are again practically independent of the temperature.

From the second linear portions sorption limits can be assessed and

it was found that in all cases the fraction of sorption attained at the time defined by the elbow point of each isotherm was 50 per cent. of the limiting value. (That this regularity had less significance than was originally supposed was shown by the fact that on repeating the experiments at a slightly later date, the elbow-points were advanced a little beyond 50 per cent. sorption, and, four years later, to nearly 75 per cent. sorption.)

It was also found that when the logarithms of the times marking 50 per cent. sorption were plotted against the logarithms of the corresponding pressures, a straight line of gradient -0.8 was obtained, so that $p^{0.8}t$ was a constant for 50 per cent. sorption.

Finally, on substituting the sorption fraction, $\frac{s}{\sigma}$ (where σ = limiting value of s) for $\log s$, and $\log p^{0.8}t$ for $\log t$, the points of nine experiments at 0° C. and under a number of different pressures, all fell on a single

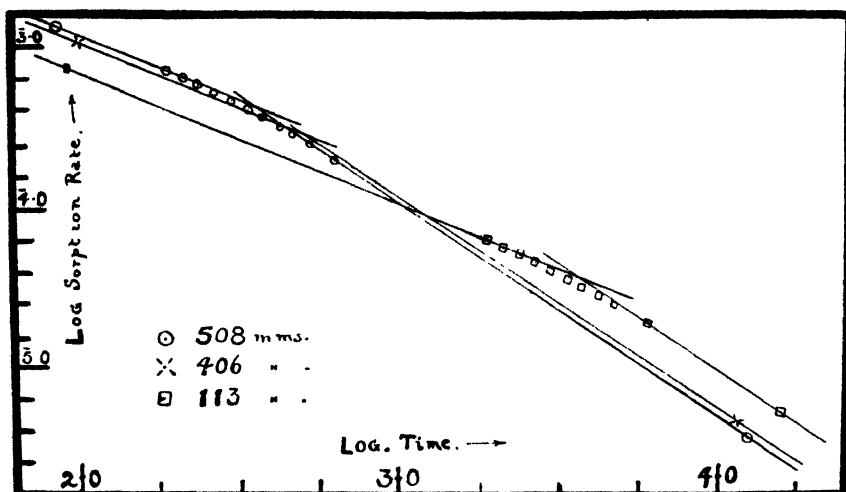


FIG. 1.

curve. That is, the sorption fraction at constant temperature is a single-valued function of the product $p^{0.8}t$.

This composite graph might have been derived from the original isotherms in two stages.

Suppose, in the first place, that we plot $\log s$, against $\log p^{0.8}t$. The effect of the introduction of the pressure term is to produce a horizontal displacement of the curves which brings them into such a position that the vertical intercepts between any pair are constant; that is, independent of the abscissa value. If now, we replace s by s/σ there is a vertical displacement and the parallel curves are superimposed.

Considering next a series of experiments carried out at different temperatures but under the same constant pressure, it was found that the sorption fraction is a function of the product of the time and a power of the absolute temperature, so that, combining all three variables we can write:—

$$\frac{s}{\sigma} = f(tp^aT^b), \text{ where } a = 0.8 \text{ and } b = 13.7.$$

In the later experiments where the elbow-points of the rate-graphs marked about 75 per cent. sorption, though the sorption fraction could still be expressed as a composite function of pressure and time, the value of the pressure exponent was now 1.5 instead of 0.8, indicating that the path of sorption towards its limit had altered appreciably. But though the course of the sorption process appears to vary greatly with the specimen of glass employed and even with the age of a particular specimen, the pressure coefficient in the limit seems to be little affected. Thus when $\log \sigma$ was plotted against $\log p$ for the early series, a slightly curved line with a mean gradient of about $\frac{1}{3}$ was obtained, and the later results yielded a figure of the same order. The pressure range in question was from 100 to 800 mm.

From the earlier experiments it was found that—selecting the half-sorption points for comparison, the rate of sorption at constant temperature was very nearly directly proportional to the pressure, and at

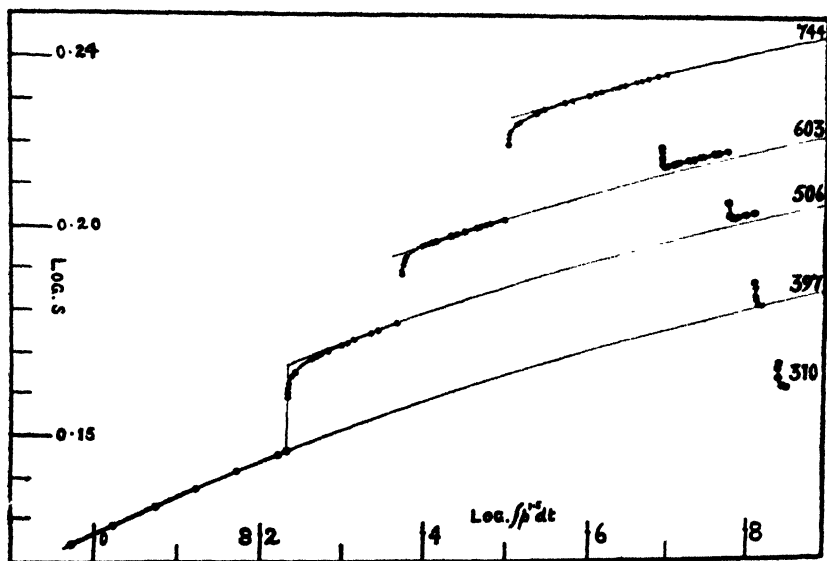


FIG. 2.

constant pressure the rate was approximately doubled for every 20° rise in temperature.

Lastly, for any constant pressure series the limiting sorption value was a linear function of the reciprocal of the absolute temperature.

There is necessarily some uncertainty about the accurate recovery of the initial condition of the sorbent after driving off the gas at the conclusion of each experiment. With the hope of eliminating this source of error, Mr. W. H. Jones (who has been extending the work of Francis and the writer) has recently conducted experiments in which the pressure has been raised periodically as sorption proceeded, and then lowered again through the same stages. At each stage the pressure was kept constant for a considerable period of time, the sorbent being maintained at the constant temperature of 0° C. Following the conclusions already arrived at $\log s$ was plotted against $\log \int p^a dt$ (a , in this

case, having the value 1.5), and a discontinuous graph was obtained. (Fig. 2.)

After each pressure increase there is a sudden jump in the sorption value which thereafter picks up its original direction. The system had been left at the initial pressure for a sufficient length of time for a limit to be evaluated and this section of the curve has been extrapolated on this basis. Now if it is legitimate to replace the pressure time function by the integral expression, then the sorption values on any selected ordinate should represent the same fractions of the saturation values for a series of pressures; that is, they should be proportional to the respective σ^2 , and curves drawn through each section of the composite graph should be parallel; that is, vertical intercepts between any pair should be constant. The diagram indicates that curves so drawn satisfy the experimental points.

From the vertical intercepts the value of $\frac{d \log s}{d \log p}$, that is, $\frac{1}{n}$ in the Freundlich equation— $s = kp^{\frac{1}{n}}$ —can be computed, and the figure so found is in very fair agreement with that obtained before.

Desorption.

Perhaps the most interesting feature of the graph is the fact that, when the pressure is reduced, the sorption value, after passing through a minimum, follows closely the course of the extrapolated sorption line appropriate to the pressure in question. By the device of raising the pressure and then dropping it to the original value we have, so to speak "cheated time," and got much further on in the sorption story than we should have got in an equal time under the original pressure.

Thus the last sorption value recorded in the graph was attained after forty-three days. If the original pressure had been 100 mm. and had been maintained constant, more than a year would have been required to reach the same value of sorption.

This same graph throws considerable light on the apparent irreversibility of sorption noticed in the case of a number of gases examined by Bangham and the writer at a much earlier date. Suppose a number of sorption experiments under increasing pressures, p_1, p_2, p_3, p_4 are continued for long periods of time so that the rate of sorption is reduced to a few c.mm. a day. If at the end of the last experiment the pressure is reduced from p_4 to p_2 , a rapid evolution of gas is observed. This soon diminishes and sorption comes to a halt at a value very much higher than the corresponding point on the sorption line. The explanation may be that the apparent equilibrium point marks a balance between slow desorption and slow continued sorption. In these cases a passage through a minimum was not actually observed because sorption had become exceedingly slow before the pressure reduction was made.

The hysteresis is maintained as the pressure is dropped to p_2 and p_1 , with the result that the gradient of the desorption line is about half that of the sorption line when $\log s$ is plotted against $\log p$.

It is possible, therefore, to explain apparent irreversibility by making appropriate allowance for slow time effects, but it would be quite impracticable in any finite time to remove all gas from the glass by isothermal reduction of the external pressure, even if this pressure reduction were carried to a high vacuum.

Thus glass which has been treated with ammonia for a week or two at atmospheric pressure still retains more than half its ammonia content after several days' exposure to the vacuum produced by charcoal cooled in liquid air.

In these experiments with glass it is difficult to decide what preliminary treatment should be given to the surface. From the point of view of the original object of the investigation it would appear that such treatment should resemble that normally given to ordinary gas apparatus: washing with alkali, nitric or chromic acid, and water, and then drying at a moderate temperature. But washing with acids may produce a roughened surface containing amorphous silica, and, as regards heat treatment, Mr. Jones has found that annealing the glass produces a particularly flat type of sorption isotherm. The water content of the glass will depend on the temperature to which it has been heated, and the period of heating, and in the case of soluble gases like ammonia the quantity taken up varies with the amount of moisture in the glass.

In general it has been found impossible to correlate the shape of the sorption isotherm either with the physical condition or the previous history of the glass.

Again, the pressure coefficient of sorption depends on the length of time for which gas and glass have been in contact and is found to have different values after equal periods of sorption with different samples of glass.

In all cases, however, it appears to tend to a limiting value of about $\frac{1}{2}$ for ammonia at 0°C . over the pressure range investigated. The quantity of carbon dioxide taken up by glass is approximately proportional to the square root of the pressure, so that this gas, though sorbed in smaller amount, is more sensitive to pressure than ammonia.

From the somewhat inconclusive data obtained so far, it would appear that the most logical procedure for minimising sorption errors in density or compressibility measurements would be to expose the glass surface to the experimental gas for a considerable period of time at the highest pressure that is to be used. On reduction of pressure variation of sorption will then occur along the flat desorption line which remains nearly constant in gradient over any reasonable finite time in spite of the fact that we are not dealing with true equilibrium conditions.

Manchester University.

THE RÔLE OF SURFACE ADSORPTION IN CHAIN REACTIONS.

BY C. N. HINSELWOOD.

Received 2nd November, 1931.

The recognition of the distinction between reactions occurring in the gas phase and those occurring at the surface of the containing vessel was one of first and most essential steps in the understanding of the kinetics of the chemical change in gases. To the two classes of reaction, homogeneous and heterogeneous, is now added another, namely that of chain

reactions in which the cycle of chemical processes constituting the so-called chain may begin at the surface of the vessel and be continued in the gas, or *vice versa*; or may begin at the surface, continue in the gas, to be finally stopped at the surface again. A chain reaction may proceed either with a steady and measurable velocity, or explosively; and it is a remarkable characteristic of many chain reactions that there exist sharply defined limits of pressure separating a region of explosive combination from a region of very slow change. Sometimes the transition from slow reaction to explosion occurs with increasing pressure, and sometimes with decreasing pressure, while in some examples both upper and lower limits can be found, outside which the reaction velocity is slow and between which it is explosively fast. It is the purpose of this paper to examine the part played by the surface of the vessel in determining both the steady reaction velocity, and the conditions of explosion.

Steady Reaction Velocity.

The rôle of the surface may be to start or to break chains. We may classify matters as follows:—

1. The chains upon which the steady reaction velocity depends may have their origin on the wall. The existence of this state of affairs, although now often assumed in given examples, is not easy to demonstrate. Thus it has been assumed that chains start on the wall in the case of the thermal decomposition of chlorine dioxide,¹ and again in the catalytic decomposition of ozone by bromine.² The principal reason for the assumption lies in the variability of the reaction rate with the exact condition or previous history of the surface of the vessel. It must be remembered, however, that chains may not only start on the wall, but may end there, and that their termination is often due to the chemical action of an adsorbed gas. An increased reaction rate, for example, may mean that the wall has become less efficient in breaking chains, and not necessarily that it has become more efficient in starting them. Thus variability of rate with surface condition is an ambiguous criterion. There is, of course, one set of circumstances which makes the wall the only possible origin of the chains, namely when the reaction is propagated from a surface, such as a hot wire, into a gas phase region where no chemical change would occur at all in the absence of the surface. When wall and gas are at the same temperature the matter becomes much more difficult to decide. We must first show that the wall does not control the rate in virtue of its stopping power: this can be done by showing that the reaction rate is not increased by increasing the linear dimensions of the free space which the chains have to traverse. Variability of reaction rate with the nature of the surface and with the nature of the gas films adsorbed on it then indicates that the reaction starts there. But the evidence that chains are propagated at all now becomes much less certain, since we might be dealing merely with an ordinary surface reaction. The decision will have to depend upon the relation between the rate and the concentrations of the various reacting gases, and the analysis of the problem becomes rather a delicate matter. A dependence of the rate upon a high power of the concentration of one of the reacting gases will indicate that propagation through the gas phases plays a part in the total process.

¹ Schumacher and Stieger, *Z. physikal. Chem.*, B, 7, 363, 1930.

² Lewis and Feitknecht, *J. Amer. Chem. Soc.*, 53, 2910, 1931.

To exemplify the difficulty of making a correct decision, we may consider the example of chlorine dioxide. The rate of decomposition varies very much with the state of the vessel wall. But since packing the vessel with glass tubes diminishes the rate of reaction very markedly, it is clear that the wall is concerned with breaking chains: whether it is concerned with starting then remains an open question. The rate of reaction varies with the square root of the chlorine dioxide concentration, and approximately with the first power of the total gas pressure. The second of these factors points to the existence of chains which diffuse to the wall. We are still left in doubt as to the place of their origin. Schumacher and Stieger found that, after a certain treatment of the vessel, it was possible to keep chlorine dioxide without reaction for a considerable time at the end of which an explosion occurred. From this they concluded that the origin of the reaction must have been the wall, since otherwise some reaction would have been observed during the induction period. While it is not at all unreasonable, this explanation does not seem to be the only possible one. If there is a very marked influence of "clean" (or of contaminated) walls in destroying some substance that is necessary for the effective propagation of the chains, then there may quite easily be a long induction period.

2. The wall breaks the chains: this case is subdivided into:—

(a) The chains upon which steady reaction velocity depends may have their origin in the gas phase and be broken at the surface.

(b) The chains may start at the surface, traverse the gas, and be broken at the wall again. This is also a sub-division of case 1, but is best considered here with 2 (a), since in both 2 (a) and 2 (b) there is observed the characteristic phenomenon that the rate of reaction depends very markedly on the dimensions of the containing vessel. For a cylindrical vessel the rate will be proportional to the square of the radius. Moreover, there will be a considerable influence of foreign gases on the reaction rate, since these impede the diffusion of the chains to the wall. The effect may, however, be masked if the foreign gas exerts any specific deactivating influence at any point in the cycle of reactions. The influence of vessel diameter is very well marked in the combination of hydrogen and oxygen,³ and in the oxidation of methyl alcohol.⁴ In the oxidation of benzene vapour⁵ it is small, indicating that the chains terminate principally in the gas phase.

Again, it is difficult to decide whether the chains start in the gas or at the wall. If the condition, as distinct from the area, of the wall could be accurately enough controlled, it would be possible from the quantitative relation between rate, area of wall, and linear dimensions of the free gas space to distinguish between the two possibilities. For, in the one, packing a vessel with narrow tubes would cut down the speed by breaking the chains, while in the other there would be a compensating increase in speed from the fact that with greater surface the number of chains starting would be increased. The two opposing effects would, however, operate according to different laws, the acceleration being proportional to the increase in surface area, the retardation being a function of the square of the diameter of the tubes. Unfortunately, however, the matter is complicated by the fact that there is nearly always an ordinary heterogeneous reaction occurring simultaneously

³ Thompson and Hinshelwood, *Proc. Roy. Soc., A*, **122**, 610, 1929.

⁴ Fort and Hinshelwood, *ibid.*, **129**, 284, 1930.

⁵ Fort and Hinshelwood, *ibid.*, **127**, 218, 1930.

with the chain reaction, and the effect of this is difficult to allow for accurately. If we can show, from the influence of vessel dimensions, that the chains are broken principally at the wall, and if we find that the reaction rate varies as a high power of the concentration of one of the reacting gases, then there is a considerable probability that the chains have their origin in the gas phase. For, we have to explain the high power of the concentration as arising from the product of two probabilities, that of the chain starting and that of its being continued through the gas. Sometimes the rate is so sensitive to concentration that we have to suppose the initial act itself to depend upon a power of the concentration of one of the reacting gases a good deal higher than the first: and this state of affairs is very much more characteristic of a homogeneous than of a heterogeneous reaction. To illustrate this argument it is instructive to compare the examples of the oxidation of benzene and the oxidation of methyl alcohol in the gaseous condition. The oxidation of benzene takes place at a rate which is nearly independent of the vessel, unless these dimensions are very much reduced, when the rate falls. Thus, normally the chains are broken in the gas phase. The rate is approximately proportional to a power of the benzene concentration between the third and the fourth. Thus there is every sign of a homogeneous change. With methyl alcohol the rate varies with the concentration in an almost exactly similar way, but the influence of the linear dimensions of the vessel is such as to show conclusively that the chains are broken at the walls. Both from the high order of reaction, and from analogy with the similar example of the benzene oxidation it appears probable that the chains start homogeneously.

In general, there is no reason why one type of process should occur to the exclusion of the other. Reactions of a non-chain character take place both homogeneously and heterogeneously, and there is nothing to prevent both gas reactions and wall reactions under the appropriate conditions giving rise to products from which chains can proceed.

Mechanism of the Breaking of Chains by the Wall.

The process by which the wall interrupts the chains may be either of the nature of a physical deactivation, or of a definite chemical reaction by which one of the entities responsible for the propagation of the chain is destroyed. A distinction can be drawn between "material" chains and "energy" chains: in the former the chains are propagated by atoms, radicles or molecules which are active in virtue of their chemical structure or unsaturation, while in the latter the chain carriers are molecules which are only active in virtue of their high energy content. Only the latter would be subject to physical deactivation. Both kinds could suffer destruction by a chemical reaction at the wall.

While it is possible that in different examples both physical and chemical deactivation play a part, and while absolutely conclusive evidence is not available, there are a number of facts which can be much more naturally interpreted in terms of the hypothesis that chemical deactivation is the commoner and more important mechanism. They are as follows:—

1. Sometimes, as in the oxidation of phosphine, it appears that the number of impacts which one of the chain propagating molecules must make with the wall before it is put out of action is very large,⁶ e.g.,

⁶ Hinshelwood and Clusius, *Proc. Roy. Soc., A*, **129**, 589, 1930.

of the order 10^5 . This is more easily understandable in terms of the chemical theory than in terms of the physical deactivation theory.

2. The deactivating power of a wall varies considerably with its exact surface condition. In particular, it may vary from experiment to experiment in a way which is sometimes very tiresome. The variations are very probably connected with changes in the gas films adsorbed on the surface, and these will influence the adsorption of that gas which reacts with the chain carriers, the chain breaking power of the wall being thus affected. If the conclusion indicated in the preceding paragraph is at all generally valid, then there is room for very large variations in the deactivating efficiency, which indeed are observed. The treatment of glass vessels with potassium chloride was, for example, found by Pease⁷ to alter the rate of reaction between hydrogen and oxygen (in the region where the chains are broken by the walls) by many times.

3. In certain reactions where the chains are known to be broken principally at the walls, one of the reacting gases is found itself to have a quite marked deactivating effect. The most natural assumption to make here is that the gas exerts its deactivating effect where the chains are known to be principally broken, namely at the wall. Since the deactivator is itself one of the reacting substances, it is not at all impossible that the very reaction which would lead to the further propagation of the chain when it occurs in the gas phase, can cause the interruption of the chain when it takes place on the wall.

In the oxidation of methyl alcohol vapour the chains are broken principally at the wall, and the rate of reaction is, under appropriate conditions, diminished by increasing the oxygen concentration. It has been found convenient to assume that the chains are broken when one of the chain propagating intermediate compounds is oxidised away by the adsorbed oxygen on the vessel wall. In the same way in the oxidation of hydrogen sulphide,⁸ where the chains seem to start in the gas and to be broken at the wall, the rate of reaction varies as a fairly high power of the oxygen concentration but decreases with increasing hydrogen sulphide concentration. It would be natural to assume here that the deactivating effect of the wall depends upon its adsorbed hydrogen sulphide, with which some oxygenated body involved in the chain reacts and is thereby destroyed.

On the other hand, it must not be supposed either that all reactions in which the chains are broken at the wall show this deactivating influence of one of the reacting substances, or that all reactions in which the deactivating influence of one of the reactants is found are characterised by wall deactivation. The oxidation of benzene is retarded by excess of oxygen, but the chains are broken chiefly in the gas. The combination of hydrogen and oxygen at higher pressures is greatly favoured by an increase in the concentration of either gas, and the chains are broken principally at the wall.

Explosion Limits.

The existence of sharp transitions from slow reaction to explosion is one of the most remarkable phenomena to which the chain mechanism can give rise. It is quite probable that the explanation of these transitions is not the same in every example. Thus it will be convenient to

⁷ Pease, *J. Amer. Chem. Soc.*, **51**, 1839, 1929.

⁸ Thompson and Kelland, *J. Chem. Soc.*, 1809, 1931.

summarise the different ways in which apparent discontinuities in the curve connecting reaction velocity and concentration can arise.

1. An explanation which made the surface of the vessel play the all-important part in determining the explosive limits was suggested by Gibson and Hinshelwood⁹ in connection with the combination of hydrogen and oxygen in presence of small quantities of nitrogen peroxide. The combination is explosive if the concentration of the latter gas lies between two sharply defined limits, but very slow if it lies outside these limits. The hypothesis was that there occurred a surface reaction involving the nitrogen peroxide, and that the rate of this reaction first increased and then decreased again as the concentration of the peroxide increased. This is a well-known type of heterogeneous reaction, in which one of the reacting gases favours the reaction at low concentrations in virtue of its mass action, but at higher concentrations acts as a poison and displaces the other reactant from the surface. If now on certain active points of the surface this hypothetical reaction attains a great enough velocity, it may generate heat rapidly enough to cause inflammation of the gas as a whole. Since the velocity passes through a maximum, there will be a concentration on either side of that corresponding to the maximum where the reaction velocity on the active points has fallen off too much to allow ignition to occur. These concentrations will correspond to the explosion limits. Since the intense local reaction which may cause the ignition is confined to certain points on the surface, its consumption of the reacting gases need not be large, and if it does not succeed in acting as a sort of detonator to the gas as a whole, it may be almost insignificant. Hence the apparent discontinuity in the reaction rate as the limits are passed.

This explanation can be transferred in principle to a reaction between two gases without the presence of a third substance like the nitrogen peroxide. There must be assumed a surface reaction, the rate of which passes through a maximum when the concentration of one of the gases is increased: the explosion limits occur at those concentrations between which the speed of the surface reaction is locally great enough to cause ignition.

Later, this explanation of the nitrogen peroxide-hydrogen-oxygen reaction was dropped in favour of Semenov's theory of branching chains.

2. The theory of branching chains¹⁰ supposes that, at the end of each cycle of chemical changes constituting a link in the chain, one original active molecule gives rise to two or more. Thus the reaction velocity will increase indefinitely, except in so far as various deactivating influences destroy the products of the successive cycles to a greater or smaller extent, and so keep the *effective* yield of activated molecules at less than one per cycle. If, with changing conditions, the effective yield passes from just below to just above unity, the reaction velocity will pass from a steady value, which may be quite small, to a value which increases in the course of a few cycles (*i.e.*, in an immeasurably short time) to an indefinitely great one. In a gaseous system at low concentration, diffusion of active molecules to the wall can lead to serious loss by deactivation, while at high concentration deactivation of active molecules by collisions in the gas phase can become important. Where the first factor just ceases to reduce the effective yield per cycle to below unity, there will be an explosion limit, the "lower limit,"

⁹ *Trans. Faraday Soc.*, **24**, 559, 1928.

¹⁰ Semenov, *Z. Physik*, **46**, 109, 1927; **48**, 571, 1928.

while where the second factor reduces the yield to less than unity once more the "upper limit" will occur. A very good example of this is found in the oxidation of phosphine, in which two limits separate a region of explosion from regions of almost immeasurably small velocity. The lower limit is influenced by the diameter of the containing tube, and by the presence of inert gases, in exactly the way which would be expected if diffusion of chains to the wall were the important governing factor,¹¹ while the upper limit is independent of the diameter of the vessel.¹²

The upper and lower limits found in the combination of hydrogen and oxygen are most satisfactorily explained in an analogous manner.

According to this theory, the exact manner in which the chains start is not of very great importance in determining the limits, the position of which is determined by the condition for effective branching of such chains as there are, rather than by the number of chains originated in unit time. In the combination of hydrogen and oxygen at not too high pressures, the chains appear to originate at the vessel wall:¹³ at the upper limit they are broken in the gas phase.³ The upper limit is the same in a porcelain vessel as in a silica vessel, the condition for branching not being affected by the difference in the nature of the surfaces from which they start. In an extreme case, with a vessel from the wall of which no chains started at all, there would naturally be no explosion and consequently no limit. If the condition of the surface is such that an extremely minute number of chains start from it, then, although theoretically the explosion limits should be found in the normal position, in practice the interference with the propagation of these few chains by such factors as fortuitous impurities may be relatively serious and the limit may suffer a certain displacement. As long, however, as an abundant supply start, the position of the upper limit will be constant. This corresponds with the experimental facts. Alyea and Haber reported a shift in the upper limit of the hydrogen-oxygen explosion region, depending on "pre-treatment" of the surface of the containing tube. These experiments were made by a streaming method, in which the concentration conditions could not have been very well defined. By a static method Garstang and Hinshelwood¹⁴ found that the displacement of the limit in porcelain vessels was very small, if real at all, while in silica vessels it could not be detected.

3. Alyea¹⁵ has called attention to another way in which the existence of an upper explosion limit can be conditioned. He suggests that in mixtures of hydrogen and oxygen above the upper limit a layer of hydrogen covers the wall of the vessel, "poisoning" it and preventing the departure from it of chains which would branch in the gas phase and give rise to explosion. As the pressure is reduced, a point is reached at which this hydrogen film is discontinuously stripped from the wall (by the attack of the oxygen). From the free wall chains now proceed in to the gas and explosion occurs.

This mechanism is a possible one in principle, though there appear to be insuperable objections to its application in the particular example.¹⁶

¹¹ Dalton and Hinshelwood, *Proc. Roy. Soc., A*, **125**, 294, 1929.

¹² Dalton, *ibid.*, **128**, 263, 1930.

¹³ Alyea and Haber, *Z. physikal. Chem.*, **B**, **10**, 193, 1930.

¹⁴ Garstang and Hinshelwood, *Proc. Roy. Soc., A*, **130**, 640, 1931.

¹⁵ Alyea, *J. Amer. Chem. Soc.*, **53**, 1324, 1931.

¹⁶ Garstang and Hinshelwood, *Proc. Roy. Soc., A*, **134**, 1, 1931.

Investigation of the kinetics of the surface reaction itself fails to reveal the presence of the complete hydrogen film; it is very improbable that such a film would be stripped off a silica surface and off a porcelain surface at the same pressure; and, finally, the fact that excess of hydrogen or oxygen can stop the explosion for any given partial pressure of the other gas proves that the limit is determined by deactivation in the gas phase.

Nevertheless, it is possible that examples of the operation of this mechanism may be found.

4. Another kind of mechanism was tentatively suggested by Hadow and Hinshelwood¹⁷ to explain a lower limit of explosion in mixtures of oxygen and cyanogen. If there is a finite rate of adsorption of the different gases admitted to the reaction vessel, and if two of the gases compete for possession of the surface, then the relative amounts of the two which are adsorbed immediately after admission to the vessel may be different from the relative amounts adsorbed a fraction of a second later, when equilibrium has been established. This is because the more rapidly adsorbed gas may momentarily take possession of a larger proportion of the surface than corresponds to its share. The rate of reaction between the two gases may at the first moment, therefore, be very different from the rate an instant later: in particular, it may be very much greater. This abnormal initial rate will not in general be perceptible, because it decays very rapidly, and may be succeeded in an immeasurably short time by a quite slow rate corresponding to the true adsorption equilibrium. If, however, this momentary rate becomes rapid enough to inflame the gas as a whole, then obviously there is no question of adjustment to the normal slow value. Thus there will be the appearance of a discontinuous passage from quite slow reaction to explosion, although there was really no discontinuity in the process actually responsible for the ignition. There is evidence that something of this kind may actually occur in the oxidation of cyanogen, but no other example is known in which the mechanism can plausibly be supposed to operate.

It is customary to draw a distinction between thermal explosions and those due to branching chains. In the former the reaction velocity is observed to increase continuously as the explosion limit is approached, until the heat produced can no longer be conducted away rapidly enough. In the latter there is the appearance of a discontinuous change at the point where the chains begin to branch effectively. Of the four mechanisms enumerated above (1), (3) and (4) really depend upon thermal explosions, the appearance of discontinuity in the reaction velocity-concentration curve being illusory and due to the fact that the explosion is conditioned by a process which is independent of the normal slow reaction, and which obtrudes itself at a point not determined by the normal reaction velocity. Mechanism (4), the branching chain mechanism, can in a more correct sense be said to represent a discontinuity in the reaction process itself. Even here, however, the discontinuity does not lie, strictly speaking, in the reaction velocity-concentration curve; it is determined by the point at which the time derivative of a very small reaction rate acquires a positive value.

¹⁷ Hadow and Hinshelwood, *Proc. Roy. Soc.*, **132**, 375, 1931.

CRITICISM OF SOME EXPERIMENTAL EVIDENCE FOR ACTIVATED ADSORPTION.

BY L. J. BURRAGE.

Received 26th January, 1932.

1. Introduction.

In view of the importance of the theory of activated adsorption it is necessary that the experimental support for this should be definitely established. Since it would appear that values for this activation energy are being deduced from results which are themselves far from correct in that they depend on false equilibria, the author has submitted this short paper in the hope that future experimental work may incorporate the changes suggested, which will certainly result in very different values for the activation energy in certain cases.

2. Discussion.

It is well established that adsorbed films cannot be completely removed by evacuation, but that treatment with a high pressure charge of gas at high temperature is much more efficient. For instance, carbon dioxide is readily removed from an evacuated charcoal by saturating with carbon tetrachloride at room temperature at approximately 1 mm. pressure and then raising the temperature to 100°. On cooling a large amount of carbon dioxide is found in the vapour phase. If this gas is pumped away and the process repeated several times, less carbon dioxide is evolved on each occasion, and equilibrium is attained much more rapidly. At the same time, the capacity of the charcoal for carbon tetrachloride increases out of all proportion to the removed gas.

This is not a new result as is instanced by the poisoning found by Benton and White.¹ Here a small amount of carbon monoxide caused a very large drop in the quantity of hydrogen adsorbed by the finely divided metal. The fact, however, that it has also a large effect on the rate of sorption seems to have been overlooked in the work on kinetics.

Burstein and Frumkin² evacuated their charcoal for twenty-seven hours at 200°, and obtained "an oxygen free charcoal surface." In this laboratory charcoals have been evacuated at 800° for very much longer times, and yet have given off appreciable amounts of carbon monoxide continuously over a long period during the subsequent investigation of a vapour isothermal. Hence, unless the surface is absolutely clean, little meaning can be attached to activation energies derived from kinetics. Again they note a dark deposit on the walls of the vessel which is "probably due to the decomposition of some hydrocarbons." This again would appear to show that the original surface was not clean, these hydrocarbons having passed into the vapour phase as the surface was flushed with hydrogen.

Harned³ found that simply heating charcoal up to 1200° in a vacuum

¹ *J.A.C.S.*, **53**, 3301, 1931.

² *J.A.C.S.*, **42**, 372, 1920.

³ This discussion.

would not suffice to produce an absolutely gas-free charcoal. He carried out experiments on the adsorption of chlorpicrin and "annealed" his charged charcoal at various high temperatures. After each treatment the amount of adsorbed vapour increased, as also the rate of adsorption, until finally a constant quantity value was attained.

If the heat of activation is calculated by the method used by Taylor and Williamson ⁴ the following formula is used :—

$$\log \frac{t_2}{t_1} = \frac{Q}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

where t_1 and t_2 are the respective times at temperatures T_1 and T_2 which are necessary for the same volume to be adsorbed. It is clear that serious errors in t_2 or t_1 will practically nullify any conclusion drawn from the experiment, and these values will depend on how clean the surface is. During the course of the experiment the surface will be cleaned up, to an extent depending on the temperature and pressure of the gas. Any residual foreign matter on the surface will affect t_2 and t_1 to varying degrees.

In the case of the adsorption of oxygen by charcoal the activation energy is determined by the slowest process occurring at the surface, the experiments of Rhead and Wheeler ⁵ indicating this to be the evaporation of the products, *i.e.*, of carbon monoxide and carbon dioxide. At higher temperatures these gases will become more mobile on the surface, and under the increased bombardment of oxygen molecules will tend to fly off and thus allow oxygen to take their places, giving rise to the observed steady drift, which is not found at low temperatures, where the carbon monoxide and dioxide remain tightly held, giving a steady poisoning effect.

Again, in Bonhoeffer and Farkas' contribution, mention is made of unpublished results by Rummel on the catalysis of the *ortho-para*-hydrogen on charcoal. Very different velocities of transformation were observed, but this was not surprising since "oxygen-covered charcoals" were employed. The authors suggest that it is possible that hydrogen-covered charcoals would behave differently. This definitely points to disturbing influences being active on the surface.

There are many instances in Professor Benton's contribution and one in particular will be mentioned. In a paper by Benton and White ⁶ on the adsorption of hydrogen by nickel the following statement was made: "In the lower temperature range the isotherms are only slightly convex towards the volume axis, and continue to rise regularly without approaching a saturation limit. In the higher temperature type, there is a large adsorption at apparently zero pressure, the curves rapidly approach a limiting value, and much more gas is adsorbed than at lower temperatures." The result is capable of explanation on the basis that if there were a trace of adsorbed foreign gas on the metal, it would poison the surface against hydrogen at lower temperatures, but would itself be turned off by hydrogen at higher temperatures, the capacity for hydrogen being increased thereby, as is well known from poisoning experiments.

It must be mentioned that the whole of the difficulties emphasised by Maxted and Hassid in the discussion on their paper can be simply

⁴ *J.A.C.S.*, **53**, 2168, 1931.

⁶ *J.A.C.S.*, **52**, 2325, 1930.

⁵ *J.C.S.*, **103**, 461, 1913.

explained on this basis, without having recourse to varying values of activation energies, etc. Finely divided nickel was heated to 250° and then outgassed. It is not possible to remove all adsorbed gas completely even at this temperature, and hence on cooling to -183° and admitting hydrogen, a certain amount will be adsorbed rapidly, and then a very slow drift will occur over a small quantity range, in some way due to the presence of foreign molecules. (This is very similar to experiments carried out in these laboratories on charcoal, the surface of which is partially covered with carbon dioxide.) At -183° , 2.5 c.c. of hydrogen were adsorbed rapidly and this figure slowly rose to 2.7 c.c. The temperature was raised in steps and the quantity of hydrogen adsorbed, determined at each pressure. At 250° , 3.6 c.c. were adsorbed. Since this is the original temperature of outgassing, and there is now a large pressure of hydrogen present, it follows that flushing out will occur to its maximum extent under the given experimental conditions. This cleans up the surface and on gradually lowering the temperature, more hydrogen is adsorbed and equilibrium rapidly set up. At -183° approximately 8 c.c. are now adsorbed. The foreign adsorbed gas which is flushed out at 250° , remains in the vapour phase as its pressure is very low compared with that of the hydrogen. A large decrease in quantity adsorbed in the presence of a very small amount of a foreign substance has been noted by many workers.

Kingman⁷ flushed his charcoal with hydrogen several times at 400° - 500° , thus removing, at any rate, some of any adsorbed foreign vapour and hence his results should be more accurate than others which have been published. He notes that the heat of activation is practically constant over the experimental range of adsorption, whereas Taylor found that the heat increased with increase in the volume adsorbed. There is a distinct probability that in the latter case the difference is due to a cleaning of the surface taking place during the course of the experiment.

3. Summary.

This discussion shows the fallacy of measuring the energy of activation by rates of sorption unless the surfaces are perfectly clean; this cannot be done by evacuation alone, but the sample must be repeatedly flushed out with the given gas at high temperature. Even then it cannot be said with certainty that the surface is completely clean and that all disturbing influences have been removed.

⁷ This discussion, p. 269.

OF THE ADSORPTION OF GASES.

SECTION II. KINETICS AND ENERGETICS OF GAS ADSORPTION.

INTRODUCTORY PAPER TO SECTION II.

BY PROFESSOR DR. H. FREUNDLICH.

Received 4th December, 1931.

When I received the kind invitation of the Faraday Society to give an introductory paper for the section "Kinetics and Energetics of Gas Adsorption," I was very doubtful whether I really was able to accept it. For I have not carried out any laboratory work on this subject for many years, and I am not therefore in a position to bring forward anything new. A very general survey is, however, sometimes quite welcome to those who are not so familiar with the subject. I hope that those to whom gas adsorption is a main theme of work will pardon me if what I have to say may seem somewhat uninteresting.

Those who first investigated gas adsorption, de Saussure, Joulin and others, noticed soon that they had to deal with true equilibrium: the amount adsorbed in equilibrium with a given pressure was the same, whether they measured with rising or falling pressures. Thermodynamic points of view may therefore be used without hesitation. It was also very early noticed that the equilibrium in pure gases is reached very quickly, generally in the course of seconds or minutes. We do not find that wide range of velocities so characteristic of chemical reactions, at least not under normal circumstances of adsorption. The fact that we have strictly reversible changes of pressure in a two-phase system containing a solid and a gas, and that these equilibria are reached quickly, is often used as a criterion of the supposition that we are really dealing with cases of adsorption, that is to say with phenomena mainly ruled by surface forces. We cannot deny that these criteria are not quite satisfactory. Such an adsorption is, for instance, hard to distinguish from the chemical equilibrium of a highly porous substance, such as a zeolite or permutite, in which practically every molecule lies on a free internal surface. We know, however, of cases where substances, chemically so inert as argon, are adsorbed and where plane surfaces, like those of mica, are able to adsorb. The similarity of these cases with those in which chemically active gases are adsorbed on the surfaces of porous substances is so great that the existence of adsorption as a surface phenomenon is very generally accepted.

If we had a property characteristic of the equilibrium on the surface and changeable with the amount of gas adsorbed, we might correlate thermodynamically the way in which it depends on the pressure p with the amount adsorbed per unit of surface u . The surface tension of the

solid σ would be such a property for example, and we might make use of Gibbs' well-known equation

$$u = - \frac{p}{RT} \frac{d\sigma}{dp} \quad . \quad . \quad . \quad (1)$$

and develop from it an adsorption isothermal. But the surface tension of a solid is not practically measurable. It is somewhat hold to assume that this surface tension behaves like that of a liquid, since the rigidity of solid systems most likely does not permit an easy smoothing out of differences in surface potential. Equation (1) is, therefore, so far not of direct interest for solid surfaces. It has, however, been used in calculating the amounts of gas adsorbed on liquid surfaces, *e.g.*, of mercury, from the lowering of surface tension at different pressures of the gas.¹ Unfortunately it has not so far been possible to test these calculated values by direct measurements of the amounts adsorbed.

Since such a thermodynamic quantity characteristic of a solid surface is wanting, we are not in a position to make any progress on the very general lines so characteristic of thermodynamic reasoning, but we are forced to consider special cases in detail.

The ideal case would be an adsorbing plane surface of a well-defined substance and a gas which does not react with the solid. The measurements would have to be extended to very low pressures, because the amounts adsorbed would be very small and the behaviour at low pressures, with the surface only partly covered with the adsorbed molecules, would be of special importance. The experiments of Langmuir² with mica as adsorbent and nitrogen and methane as gases come very near to this ideal, although the chemical character of mica is not very simple, and we therefore have no assurance that the surface is really chemically homogeneous. I saw similar experiments with a very sensitive manometer being carried out in the laboratory of Stern.

This leads further to the question: how does change in the chemical nature of the adsorbent (and of the adsorbed gas) vary the behaviour of adsorption. As is well known, metals seem to behave towards gases in a very special way. It is therefore not clear how far it is permissible to generalise experiments with metal. I might, however, mention here that the adsorption of gases like hydrogen and nitrogen on metals such as nickel, molybdenum, etc., has been investigated with the help of the diffraction of electrons.³ It seems as if the atoms of these gases were bound on the surface in a regular pattern, depending upon the space-lattice of the metal.

Now we may change the surface in two ways: (1) by keeping it plane but giving up the chemical homogeneity and assuming that there are a great number of points on the surface of a different adsorbing activity than the rest; (2) by keeping the surface chemically homogeneous but making it rough and porous.

The above-mentioned experiments of Langmuir with mica are perhaps of the first kind. This conception has been used further in seeking an explanation of the behaviour of catalysts. Thus, for instance, the fact that the strongest catalytic activity is not very often found with

¹ Iredale, *Phil. Mag.* (6), **45**, 1088, 1923; **48**, 177, 1924; **49**, 603, 1925; Volmer and Mahnert, *Z. physik. Chem.*, **115**, 239, 1925; H. Cassel and Salditt, *Z. physik. Chem.*, **155 A**, 231, 1931.

² J. Amer. Chem. Soc., **40**, 1361, 1918.

³ Davison and Germer, *Physic. Rev.* (2), **30**, 705, 1927; E. Rupp, *Ann. Physik* (5), **5**, 453, 1931.

chemically homogeneous surfaces, but in presence of certain impurities in the surface of substances which have been called promoters, is assumed to be due to the fact that the catalytic reaction takes place on those parts of the surface where molecules of different kind touch one another.⁴

Undoubted examples of the second case have, however, not been investigated, in so far that we do not know whether we are really dealing with chemically homogeneous surfaces in the many cases of rough surfaces which have been used for adsorption experiments. That the roughness of a given surface is of great importance follows, however, from an experiment by Frazer, Patrick and Smith.⁵ They compared the adsorption of the vapour of toluene on a freshly blown glass surface (which may be assumed to be practically smooth) with the adsorption on the same surface after it had been roughened by treatment with cleaning solutions. The influence of this treatment was very great: on the smooth surface the amount adsorbed was not measurable, on the rough surface it was marked.

It is obvious that the roughness of the surface makes the adsorbing surface much larger. But it means further that we have on the surface a large number of cavities of very small radius of curvature. We have extreme cases of such roughness in adsorbents such as charcoal or silica gel, where the adsorbing surfaces are only separated from one another by extremely fine capillaries. The second influence of roughness just mentioned makes itself felt most strongly, if we pay regard not only to the non-condensable gases but also to the vapours. A concave surface has a lower vapour pressure than a plane one according to the formula of W. Thomson

$$p_w = p - \frac{2\sigma\rho_d}{\rho_l r} \quad . \quad . \quad . \quad . \quad (2)$$

here p_w is the vapour pressure of the surface with a radius of curvature r , σ and ρ_l are the surface tension and the density of the liquid, and ρ_d the vapour density. It has therefore been assumed that the adsorption, at least of gases below their critical point, on rough surfaces and in porous adsorbents consists in a condensation of the vapours according to this formula.⁶ We cannot calculate the adsorbed amounts absolutely in this way, for we know nothing about the values of r . An attempt has been made to calculate r from the equilibrium pressures of adsorption; but the difficulty arises here that we do not know whether, in the very fine capillaries with which we are dealing (perhaps of only a few $\mu\mu$ diameter), the values of the density ρ_l and especially of the surface tension are the same as for the liquid in mass.⁷ In any case, this theory is of interest as a second way of introducing thermodynamic reasoning into the interpretation of the isothermal behaviour of gas adsorption.

⁴ E.g., H. S. Taylor, *J. phys. Chem.*, **30**, 145, 1926; H. Cassel, *Naturwissenschaften*, **14**, 103, 1926; G. M. Schwab and E. Pietsch, *Z. physik. Chem.*, **1B**, 385, 1928; **2**, 266, 1929; *Z. Elektrochem.*, **35**, 135, 573, 1929; Pietsch, Kotowski and Frl. Berend, *Z. physik. Chem.*, **5B**, 1, 1929; E. Pietsch, *Z. Elektrochem.*, **35**, 366, 1929.

⁵ *J. phys. Chem.*, **31**, 897, 1927.

⁶ See, for instance, Zsigmondy, *Z. anorg. Chem.*, **71**, 356, 1911; Zsigmondy, Bachmann and Miss Stevenson, *ibid.*, **75**, 189, 1912; Bachmann, *ibid.*, **79**, 202, 1912; T. S. Anderson, *Z. physik. Chem.*, **88**, 191, 1914; Patrick, *Koll. Z. (Zsigmondy, Festschrift)*, **36**, 272, 1925, and many other papers by Patrick and his co-workers.

⁷ P. Kubelka (*Koll. Z.*, **55**, 1, 1931), has made use of formula (2) for the adsorption of vapours by active charcoal, assuming higher values of the surface tension in the capillaries.

$$a = \alpha p^{1/n} \quad . \quad . \quad . \quad . \quad . \quad (3)$$
$$a = \frac{\kappa\lambda\mu}{I + \lambda\mu} . \quad (4)$$

* See, e.g., Polanyi, *Ber. deut. physik. Ges.*, 16, 1012, 1914; 18, 55, 1916; *Z. Elektrochem.*, 26, 370, 1920.

with rising temperature. In this way we find adsorption isosteres, curves which are similar to the vapour-pressure curves of a given solution; the pressure rises rapidly with rising temperature. (3) We may keep the pressure constant and investigate the adsorption isobars, that is the change of the amounts adsorbed with change of temperature. In Figs. 1 to 3 types of such curves are represented.

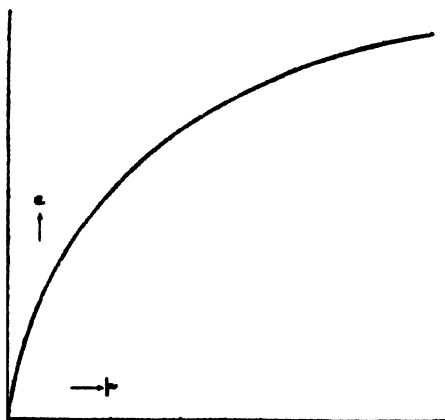


FIG. 1.

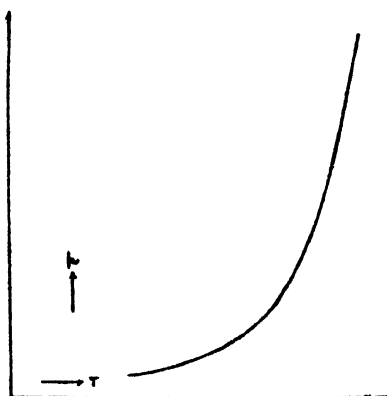


FIG. 2.

The adsorption of gases decreases as a rule with rising temperature. According to the principle of van't Hoff and Le Chatelier it ought therefore to take place with development of heat. This is indeed the case. We are able to correlate the temperature coefficient of adsorption with this heat in a manner similar to that adopted, for instance, in the well-known formula of Clapeyron and Clausius, for the temperature coefficient of vapour pressure and the heat of condensation. But since in the case of adsorption both phases have a variable concentration, the conditions are not so simple, and it needs a rather subtle definition of the quantities used. I therefore shall only mention one case, which also has been tested experimentally. E. Hückel⁹ has developed from this point of view a formula

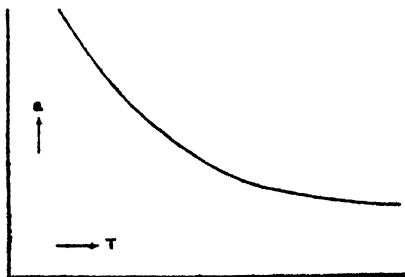


FIG. 3.

$$q + RT = RT^2 \left(\frac{d \lg p}{dT} \right)_\tau \quad . \quad . \quad . \quad (5)$$

q is the molar differential heat of adsorption measured at a constant volume and $\left(\frac{d \lg p}{dT} \right)_\tau$ the temperature coefficient of the logarithm of the equilibrium pressure under isosteric conditions. This formula may be tested by experiments of Titoff,¹⁰ although they do not quite

⁹ *Adsorption und Kapillarkondensation*, Leipzig, 1928, p. 43.

¹⁰ *Z. physik. Chem.*, 74, 641, 1910.

agree with the assumptions of the formula: Titoff did not keep the volume strictly constant when measuring q . But the uncertainty caused by this only amounts to a few hundred calories per mol., whereas the normal molar heats of adsorption are about ten times greater. The agreement is fairly satisfactory as is shown by the following table:—

TABLE I.

Gas.	a (Millimols per g. Charcoal).	q (obs.) (Cal. per Mol.).	q (calc.).
N_2	0.5	4550	3900
CO_2	2.3	6500	6500
NH_3	4.0	7900	7750-8200

If we compare the molar differential heats of adsorption for different values of the amount adsorbed a , Titoff's values seem to show that q decreases regularly with rising a . But this is not always the case. Other experiments lead to the conclusion that the molar differential heat of adsorption is very much greater (up to 20,000 calories and more) for the first small amounts adsorbed and the change with rising values of a may be complicated, having, for instance, a minimum and a maximum.¹¹

Just as in the case of evaporation, so also in that of adsorption, the equilibrium has to be considered as a dynamic one. The time during which the molecules, being interchanged from one phase to the other, dwell in the surface is therefore of great importance. This time depends not only upon the movement normal to the surface but, in the case of adsorption, very markedly on their movement in the surface itself. The existence of such a movement has been shown by experiments of Volmer.¹²

So far it was understood that the equilibrium of adsorption is reached quickly. Now there are a great number of cases where a loose combination of solid and gas is formed, but not quickly. In many cases a considerable percentage of the amount bound to the solid is taken up in a short time, but it may be hours or days before an equilibrium is reached. A general explanation of this behaviour is not known, and it is doubtful whether it would hold. When the adsorbents are very porous it is possible that we are dealing with a true adsorption, the anomalous behaviour being caused by some pores which are extremely fine; it may therefore last a long time, till the gas reaches those parts of the surface which communicate with the atmosphere outside by these pores. In other cases it is assumed that we have to distinguish between a true adsorption and a solution or absorption of the gas in the interior of the solid, the former taking place quickly, the latter slowly. McBain¹³ calls the whole phenomenon sorption, and he has investigated a few cases, which seem to agree with this assumption satisfactorily; e.g., the sorption of hydrogen by cocoanut charcoal.

Recently, cases of a rather different character have been found, which have been considered as examples of adsorption, although they

¹¹ E.g., Beebe and H. S. Taylor, *J. Amer. Chem. Soc.*, **46**, 43, 1924; A. Magnus and Kaelberer, *Z. anorg. Chem.*, **164**, 345, 1927; Polanyi and Wilke, *Z. physik. Chem.*, **132**, 371, 1928.

¹² Volmer and Estermann, *Z. Physik*, **7**, 13, 1921; Volmer and Adhikari, *ibid.*, **35**, 170, 722, 1925; Moll, *Z. physik. Chem.*, **136**, 183, 1928.

¹³ *Phil. Mag.* (6), **18**, 916, 1909; *Z. physik. Chem.*, **68**, 471, 1909.

differ distinctly from the regular cases of adsorption, also, in regard to the velocity with which equilibrium is reached.¹⁴ If hydrogen is adsorbed on metals like Ni, etc., or on oxides such as MnO, etc., we have at low temperatures an adsorption isobar agreeing with a molar heat of adsorption of the usual magnitude, that is to say of a few thousand calories. At higher temperatures the amount adsorbed rises, the equilibrium is reached in a much longer time, and so we pass on to an isobar of similar form but lying above the isobar for low temperatures. This isobar would agree with much higher values of the heat of adsorption. It is possible that we are dealing with adsorption in the whole range of temperatures, the gas being transformed chemically on the surface at higher temperatures, although it is perhaps difficult to exclude the possibility of the formation of some surface compound between gas and solid at higher temperatures.

It is a question of especial importance in this connection how far a dissociation of gases like hydrogen, oxygen, etc., takes place in the adsorption layer. According to experiments of Langmuir,¹⁵ hydrogen atoms are adsorbed more strongly than hydrogen molecules on some surfaces. This would bring about a dissociation of the hydrogen molecule into its atoms in the adsorption layer of these surfaces. For it is a thermodynamical consequence that a chemical equilibrium on a surface is shifted in favour of those substances which are adsorbed more strongly.¹⁶ This question leads us further to the problem of the mutual transformation of *ortho*-hydrogen into *para*-hydrogen, so strongly and characteristically depending upon the nature of adsorbent and upon temperature.¹⁷

There are many unsolved questions concerning the adsorption of pure gases. It is therefore easily understood that our knowledge as to the adsorption of gas mixtures is yet smaller, and that the task of delving into the intricacies of the surface grows very much harder. On the other hand, the adsorption of gas mixtures is especially important, since many practical cases, *e.g.*, those of catalysis, are concerned with them. The following facts seem to be well established: Equilibrium is reached as a rule much more slowly than in pure gases. The amount adsorbed of one gas in equilibrium with a given partial pressure is smaller in the mixture than the amount in equilibrium with the same pressure in the pure gas; that is to say, one gas displaces the other. This displacement depends largely on the power of adsorption of the pure gas; a highly adsorbable gas displaces more strongly than a weakly adsorbable one. The influence of poorly adsorbable gases such as O₂ and N₂ on the adsorption of strongly adsorbable ones, such as Cl₂, etc., is therefore negligible.

I hope I have covered in this paper the main experiences on the adsorption of gases, and have given you the most simple and reliable conclusions to be drawn from these experimental facts.

Berlin—Dahlem,

Kaiser Wilhelm-Institut für physikal. Chemie.

¹⁴ H. S. Taylor, *J. Amer. Chem. Soc.*, **53**, 578, 1931; *Z. physik. Chem., Bodenstein-Festband*, p. 475, 1931; H. S. Taylor and A. T. Williamson, *J. Amer. Chem. Soc.*, **53**, 2168, 1931.

¹⁵ *J. Amer. Chem. Soc.*, **34**, 1310, 1912.

¹⁶ See also Polanyi, *Z. Elektrochem.*, **27**, 142, 1921.

¹⁷ Bonhoeffer and Harteck, *Z. physik. Chem.* **4B**, 113, 1929; Bonhoeffer and A. Farkas, *ibid.*, **12**, 231, 1931.

ADSORPTION AND SOLUTION OF GASES BY METALS.

BY ARTHUR F. BENTON (*Virginia*).

(Received 3rd December, 1931.

The very large specific adsorptions shown by charcoal and silica made these the favourite substances, and for many years almost the only substances employed in studies of gaseous adsorption. Considerable success has been achieved in organising the data obtained with such materials under a single theoretical treatment. The theories which are found to be most applicable here are based on the assumption that the configuration of the molecule is essentially unchanged in the adsorption process, and that the forces involved are of the van der Waals' type. In so far as these assumptions are valid, the heat of adsorption should be small and, for different gases on a given solid, in the order of the heats of vaporisation. Further, it can be concluded that roughly equal quantities of different gases would be adsorbed at temperatures and pressures which are equal fractions or multiples of the critical temperature and critical pressure, respectively. These deductions have been approximately confirmed by a large mass of experimental material, for the most part on charcoal.

However, even with unreactive materials like charcoal, certain gases are much more extensively adsorbed than would be predicted from their boiling-points, and their heats of adsorption are exceptionally high. A notable example is the system, oxygen-charcoal.¹

The numerous studies, particularly in the last decade, of the adsorption of gases by catalytically active solids, such as metals and metallic oxides, have furnished many new cases of such "exceptional" adsorptions. A single example will suffice. Langmuir² found that tungsten took up oxygen strongly even at 1500° and low pressures, and showed by ingenious experiments that the process was one of surface adsorption, and not solubility or the formation of an oxide of tungsten. Selective adsorptions of this kind were given different names by different workers. Thus, "chemical," "primary," "activated," etc., adsorptions were distinguished from "physical," "secondary," or "molecular" adsorptions, respectively. In spite of the multiplicity of terms, the concept has always been the same, that there exists a wide range of adsorption phenomena which are more or less distinct from the van der Waals' type, and which are characterised by much stronger binding forces, larger heats of adsorption, and an increased reactivity of the adsorbed gas.

While it was thus recognised that different systems exhibit a wide variation in the strength of the adsorptive binding, it was commonly

¹ See, for example, Rhead and Wheeler, *J. Chem. Soc.*, 103, 461, 1913; Lowry and Hulett, *J. Am. Chem. Soc.*, 42, 1408, 1920; Blench and Garner, *J. Chem. Soc.*, 125, 1288, 1924.

² Langmuir, *J. Am. Chem. Soc.*, 38, 2221, 1916; Langmuir and Kingdon, *Physic. Rev.*, 24, 570, 1924.

supposed that any given system was endowed with only a single type of binding force and, therefore, could show adsorption of only a single type. The opposite view was proposed by Benton, and shown to be strongly supported by the results of an extensive study, in Professor Taylor's laboratory at Princeton, of the adsorption of gases by a number of oxides of widely differing catalytic activity.³

Table I. gives the adsorption ratios obtained at one atmosphere pressure for different pairs of gases on the series of oxides.

TABLE I.—ADSORPTION RATIOS FOR DIFFERENT GASES.

Ratio.	Co ₂ O ₃ .	CuO + MnO ₂ .	CuO.	MnO ₂ .	Fe ₂ O ₃ .	SiO ₂ .
$\frac{\text{CO at } -79^\circ}{\text{O}_2 \text{ at } 0^\circ}$	23	19	23	20	20	14
$\frac{\text{CO at } -79^\circ}{\text{CO}_2 \text{ at } 0^\circ}$	0.59	0.76	0.65	0.80	0.55	0.63
$\frac{\text{CO at } 0^\circ}{\text{O}_2 \text{ at } 0^\circ}$	—	18	13	5.6	3.3	1.8
$\frac{\text{CO at } -79^\circ}{\text{CO at } 0^\circ}$	—	1.06	1.77	3.64	6.00	7.92

From the approximate constancy of the ratios of carbon monoxide at -79° to carbon dioxide at 0° and to oxygen at 0° , it was concluded that all these cases represent essentially the non-selective, or van der Waals' type of adsorption. On the other hand, the large differences in the ratios of the monoxide at 0° to oxygen at 0° bring out clearly the specific nature of carbon monoxide adsorption at this temperature. The behaviour of hydrogen was similar to that of carbon monoxide. Further evidence was obtained from the behaviour on evacuation, which showed that the gas could be readily recovered, without heating, in all cases where the adsorption was of the non-selective type, but only with great difficulty in cases of selective adsorption. *Thus carbon monoxide was found to be held loosely at -79° , and extremely strongly at 0° on active oxides.* In several cases a slight reduction of the oxide occurred, but this was shown not to affect the conclusions drawn, since nearly the whole of the adsorbed carbon monoxide or hydrogen was ultimately recovered as such. Further, although a slow solution of oxygen and carbon dioxide was sometimes observed at higher temperatures, it was definitely established that no appreciable part of the adsorptions here reported could be ascribed to solubility.

These experiments demonstrated that two types of adsorption could be sharply distinguished, even in the same system—a van der Waals' adsorption common to all gas-solid systems, and a selective adsorption characteristic of the given system. It was proposed further that the two types occur together under suitable conditions, giving two simultaneous equilibria. The fact that silica showed no evidence of selective adsorption of carbon monoxide even at much higher temperatures, was made the basis of a method of calculating for each of the other oxides the contribution to the total observed adsorption at 0° furnished by each of the

³ Benton, *J. Am. Chem. Soc.*, **45**, 887, 900, 1923.

two types. Thus the van der Waals' adsorption of the monoxide at 0° was obtained by multiplying the oxygen adsorption at this temperature by 1.8 (see Table I., row 3). The remainder, which was in most cases the major part of the total adsorption, represented the selective type.

The success of the work described above depended largely on carrying the measurements to lower temperatures where selective adsorption was absent. Benton and White⁴ extended this method still further in a study of the adsorption of hydrogen by nickel. Below -190° the adsorption was entirely of the van der Waals' type, which decreased rapidly with increasing temperature. Near -190° selective adsorption first appeared, and then increased to a maximum at about -100°. In addition to the difference in the temperature ranges over which the two types are mainly manifested, the isotherms for the two cases show striking differences. In the lower temperature range the isotherms are only slightly convex toward the volume axis, and continue to rise regularly without approaching a saturation limit. In the higher temperature type, on the other hand, there is a large adsorption at apparently zero pressure, the curves rapidly approach a limiting value, and *much more gas is adsorbed* than at the lower temperatures.

More recently a number of other cases have been reported, in which the two types of adsorption were similarly identified. These include the adsorption of hydrogen and carbon monoxide by mixed catalysts of zinc and chromium oxides,⁵ of hydrogen on manganous oxide surfaces,⁶ and of carbon monoxide by palladium.⁷ Several additional examples from unpublished work in the Virginia laboratory will be presented in this paper. All of these cases show that at sufficiently low temperatures a typical van der Waals' adsorption occurs. There can be no doubt that all systems in which only selective adsorption has so far been observed, will behave similarly at low temperatures.

Taylor⁸ has recently presented an admirable summary of existing experimental data relative to the two types of adsorption, and has particularly called attention to the slow rate of selective adsorption, increasing with increasing temperature, as expressed in terms of an "activation energy" of adsorption. This point of view has lately been called in question,⁹ on the ground that gases may dissolve in solids, at least at higher temperatures, and that the rate of solution increases with temperature. While the examples already cited leave no doubt of the existence of selective adsorption, it must be recognised that a slow rate is not of itself a unique indication of this process, and that complications due to solubility may be anticipated in individual cases.

Practically all previous attempts to differentiate adsorption and solubility have been based on the assumption that the former process is extremely rapid, but this method cannot be generally applicable if selective adsorption can also be slow. In the new experiments on the sorption of gases by metals to be described below, it has been found that solubility is a frequent concomitant of selective adsorption. It will appear that these two processes can usually be distinguished when sufficient data are available on both rates and equilibria; the distinction

⁴ Benton and White, *J. Am. Chem. Soc.*, **52**, 2325, 1930.

⁵ Garner and Kingman, *Nature*, **126**, 352, 1930.

⁶ Taylor and Williamson, *J. Am. Chem. Soc.*, **53**, 2168, 1931.

⁷ Taylor and McKinney, *J. Am. Chem. Soc.*, **53**, 3604, 1931.

⁸ Taylor, *J. Am. Chem. Soc.*, **53**, 578, 1931; see also *Chem. Reviews*, **9**, 1, 1931.

⁹ Steacie, *J. phys. Chem.*, **35**, 2112, 1931; Ward, *Proc. Roy. Soc.*, **133A**, 506, 522, 1931.

becomes certain when the experimental conditions can be so chosen that the two equilibria are simultaneously approached from opposite sides.

In what follows it will frequently be necessary also to distinguish between the two types of adsorption. What have been called "van der Waals' adsorption" and "selective adsorption" will hereafter be referred to as "physical" and "activated" adsorptions, respectively, in the belief that these terms are more expressive, and less open to objection than the many others which have been proposed.

The apparatus, procedure, method of determining free space by means of helium, and other experimental details have already been described.⁴ All volumes have been reduced to standard conditions.

Sorption by Copper.

The results to be summarised here were obtained¹⁰ with an active sample of copper (Cu II, 51.51 g.), prepared by reduction of the oxide

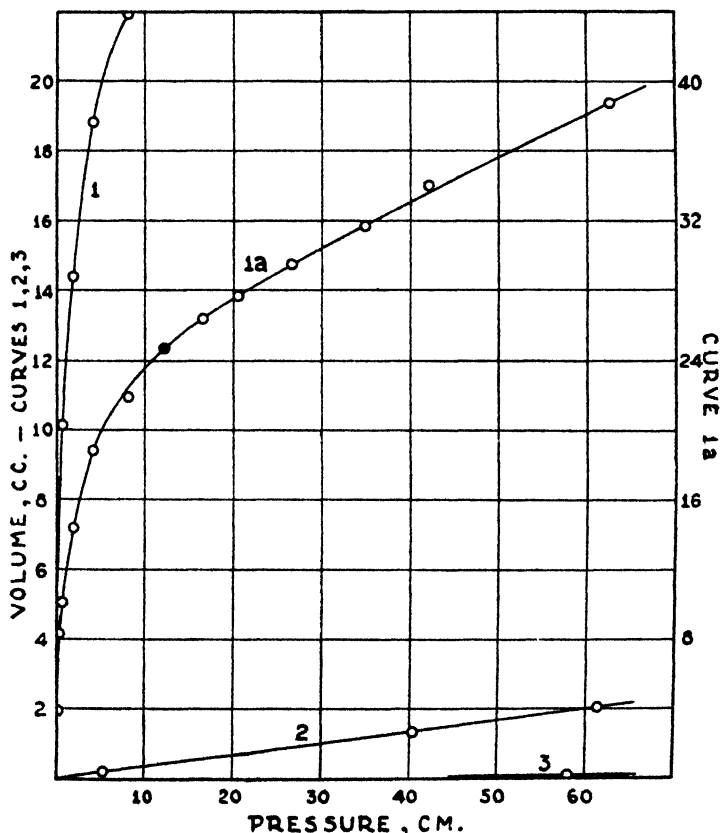


FIG. 1.—Isotherms for Nitrogen on Copper. Curves 1, 1a: -183° , Curve 2: -78.5° Curve 3: 0° .

with hydrogen, mainly at 115° and finally at 140° . Check runs at frequent intervals revealed that no change in adsorptive capacity occurred during these measurements.

Nitrogen.—Fig. 1 shows the isotherms obtained for nitrogen at

¹⁰ Benton and White, to be published shortly.

several temperatures. Curve 1*a* is a plot on a reduced scale of the complete isotherm at -183° , the first part of which is given in Curve 1. In this and following figures points designated by ordinary circles were obtained by proceeding from lower to higher pressures; black circles indicate the reverse order of procedure.

These results exhibit all the typical characteristics of physical adsorption. Thus (1) equilibrium is reached from either side practically instantaneously, (2) there is no adsorption at "zero" pressure, (3) the isotherms do not approach a saturation limit, and at the higher temperatures are approximately straight lines, (4) the adsorption at a given pressure decreases uniformly with increasing temperature, giving a relatively small heat of adsorption, which is calculated to be in the neighbourhood of 4000-2000 cal. (The latent heat of vaporisation of nitrogen is 1380 cal.)

Hydrogen.—The isotherms for hydrogen at low temperatures are plotted in Fig. 2. Apart from the marked discontinuities, which have

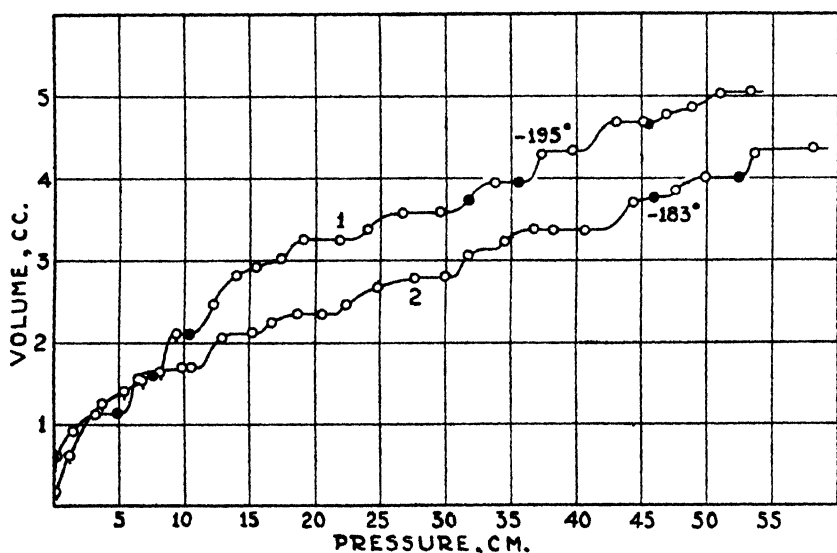


FIG. 2.—Isotherms for Hydrogen on Copper at Low Temperatures.

been treated in detail elsewhere,¹¹ these curves exhibit all the usual characteristics of physical adsorption. As with nitrogen, equilibrium is established with great rapidity and the isotherms continue to rise without approaching a final limiting value. The heat of adsorption calculated from the isotherms is about 1000 cal. At -195° there is no adsorption at zero pressure, but at -183° about 0.5 c.c. was taken up under these conditions. It will be clear from what follows that this 0.5 c.c. represents an *activated* adsorption on the most active parts of the surface. This need not mean that activated adsorption occurs at -183° , but rather that the first quantity of gas was admitted to the highly evacuated copper before the latter had had time to attain the temperature of the liquid oxygen bath. In fact, in another experiment at this temperature, where a longer time was allowed for thermal

¹¹ Benton and White, *J. Am. Chem. Soc.*, **53**, 2807, 3301, 1931.

equilibrium to be reached, there was no adsorption at zero pressure, and the entire isotherm lay quite uniformly 0.5 c.c. below Curve 2 of Fig. 2.

The isotherms for hydrogen on copper at higher temperatures are shown in Fig. 3, Curves 1 and 2. It is evident that the process occurring at -78.5° and at 0° is fundamentally different from the physical adsorption at low temperatures. At the higher temperatures the volumes taken up are much larger, there is a large adsorption at apparently zero pressure, and there is a tendency to approach an early saturation limit, especially noticeable at -78.5° . Furthermore, *extremely slow rates are now observed*, so that even after many hours values obtained from higher and from lower pressures are not in complete agreement.

Certain peculiarities of the observed results lead to the suspicion that more than one process is taking place at these higher temperatures. In the first place, the isotherm for 0° shows little tendency to approach a saturation limit, and above about 500 mm. actually gives higher values than at -78.5° . Secondly, over certain ranges of volume, the rate is even slower at 0° than at -78.5° . At the latter temperature a plot of volume versus time shows that the rate decreases continuously and uniformly from the beginning, and equilibrium is closely approached after six to eight hours. At 0° , on the other hand, a large fraction of the gas is taken up almost instantaneously, but then a sharp decrease of rate occurs, and the last portions of gas are taken up with extreme slowness.

That two different processes are in fact involved at these temperatures is conclusively shown by the following experiments. Hydrogen was allowed to come to approximate equilibrium with the adsorbent at -78.5° and a given pressure. On then bringing the system rapidly to 0° , it was found that the pressure increased far more than the amount corresponding to the change in temperature of the free space, so that considerable gas was desorbed. Subsequently, however, a slow decrease of pressure occurred, which continued until the amount of gas taken up was approximately the same as in an ordinary experiment at 0° . On then cooling to -78.5° , additional gas was taken up, and this increased value, as compared with an ordinary experiment at -78.5° , was very nearly equal to the amount taken up slowly at 0° . On again heating to 0° , no minimum occurred, but the volume quickly decreased to the normal value at this temperature.

With the value of 1000 cal. for the heat of physical adsorption, it can readily be shown that the amount of physically adsorbed gas cannot exceed a few tenths of a cubic centimeter at these temperatures. Consequently, the evolution of gas on first warming from -78.5° to 0° , which amounted to several cubic centimetres, clearly shows that the *activated* adsorption decreases markedly in this temperature range. The slow resorption that ensued is obviously a process different from activated adsorption, and may provisionally be ascribed to solution. On cooling to -78.5° the dissolved gas remains "frozen" within the solid, but at the same time the activated adsorption gradually returns to its normal value, with the result that the new value for the total sorption is greater than the amount originally obtained at this temperature, and the increase is equal to the amount which was slowly dissolved at 0° .

Thus in each such experiment, the volume slowly taken up at 0° and the increased sorption after returning to -78.5° furnish two measures of the amount of gas dissolved at 0° . Of these, the second measure should be the more reliable. The dissolved amounts thus obtained in a series

of experiments at different pressures are plotted as Curve 4 of Fig. 3. Although the slow solution process at 0° was followed for more than fifty hours, final equilibrium was never attained, and the true solubilities must, therefore, be greater than the values given by Curve 4. Nevertheless, it is worth noting that the amounts actually dissolved are roughly proportional to the square root of the pressure. It should be added that if, as seems probable, very small amounts of gas are dissolved even at -78.5° , these amounts should be added to the values shown in Curve 4.

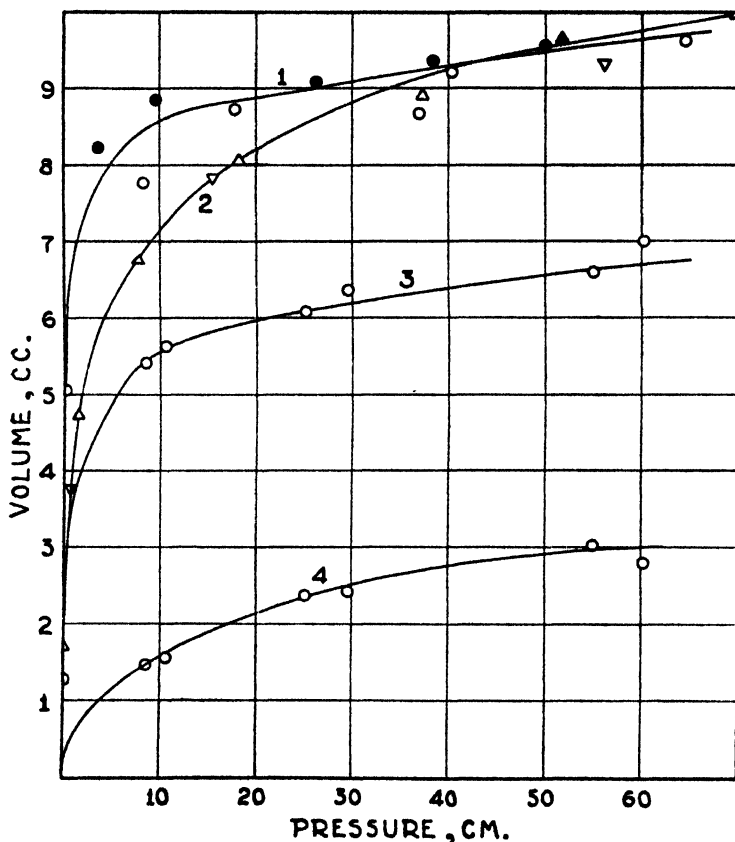


FIG. 3.—Isotherms for Hydrogen on Copper. Curve 1: Total Sorption at -78.5° , Curve 2: Total Sorption at 0° , Curve 3: Activated Adsorption at 0° , Curve 4: Solution at 0° .

When the dissolved gas is subtracted from the total sorption at 0° , Curve 3 of Fig. 3 is obtained for the activated adsorption. Although direct evidence is lacking, the assumption of a slight solubility at -78.5° , in amounts proportional to the square root of the pressure, would reduce the values shown in Curves 1 and 3, so that the activated adsorption at each of these temperatures would approach a definite saturation limit.

With the slow process at 0° accounted for as solubility, it can now be definitely stated that the rate of activated adsorption at this temperature is very rapid, while at -78.5° it is slow and conveniently measurable. At -183° the rate is apparently zero. In line with this is the

observation that when hydrogen was allowed to come to approximate equilibrium at -78.5° , and the system then rapidly cooled to -183° , the gas adsorbed in the activated form was not evolved, but on the contrary an increased adsorption occurred, doubtless corresponding to the partial formation of a layer of physically adsorbed molecules on top of the activated hydrogen.

The essential features of the results obtained for the system, hydrogen-copper, are collected in Fig. 4, which represents the 500 mm. isobars for physical adsorption (Curve 2), for activated adsorption (Curve 3), for

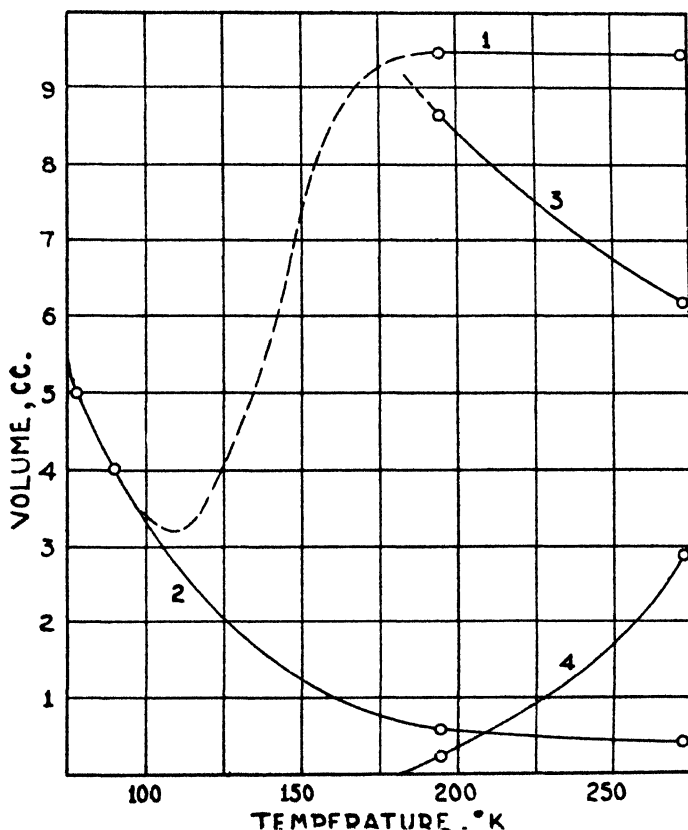


FIG. 4.—Isobars for Hydrogen on Copper at 500 mm. Curve 1: Total Sorption. Curve 2: Physical Adsorption, Curve 3: Activated Adsorption, Curve 4: Solution,

solution as observed (Curve 4), and for the total observed sorption (Curve 1), which is the sum of Curves 2, 3 and 4.

Carbon Monoxide.—The isotherms for carbon monoxide at several temperatures are given in Fig. 5, Curves 1, 2, 3, 4. Curve 1a is a reduced-scale plot of the complete isotherm at -183° , the first part of which is indicated in Curve 1. At the two lower temperatures equilibrium was reached practically instantaneously. At 0° almost the whole of the gas was taken up immediately, but this was followed by another process which was so extremely slow that only 0.4 c.c. of gas were sorbed in this way in the seven days needed to complete the isotherm shown in Curve 3. At 110° the two processes were again revealed, but here the slow

process was much faster than at 0° and involved much larger quantities of gas. Since no final equilibrium was reached, even in twelve days, the values obtained are indicated by a dashed curve (Curve 4). Curve 5 shows the amounts of gas which were taken up rapidly at 110° , that is, within about two minutes.

A casual examination of these results might suggest that the rapid process observed at each temperature is pure physical adsorption, and that the slow process represents activated adsorption. There is, however, strong evidence that three different processes are occurring. The large adsorptions at "zero" pressure at -78.5° and 0° , the comparatively small decrease in adsorption between these two temperatures, and the fact that the values are higher than those for nitrogen (Fig. 1) by one or

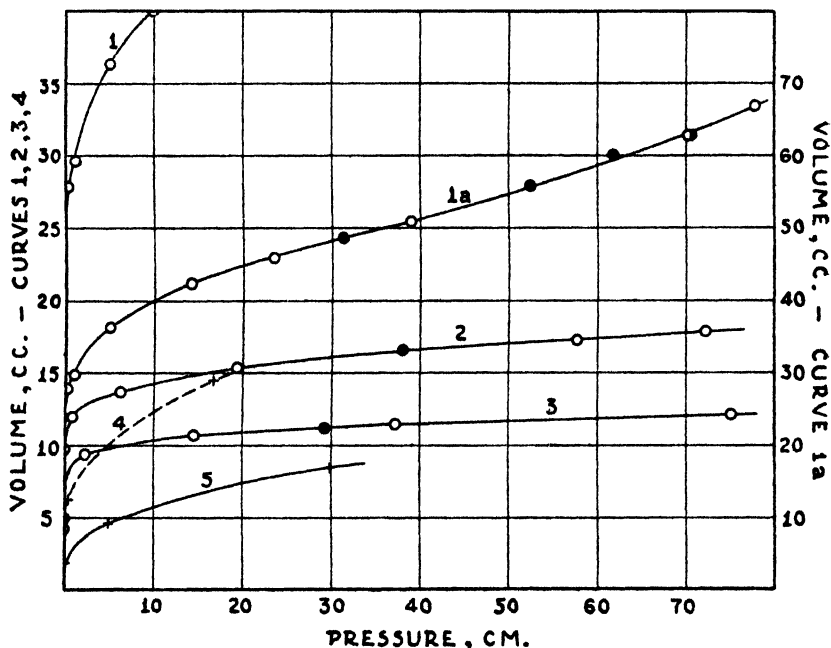


FIG. 5.—Isotherms for Carbon Monoxide on Copper. Curves 1, 1a: -183° , Curve 2: -78.5° , Curve 3: 0° , Curve 4: Final Values at 110° , Curve 5: Immediate Adsorption at 110° .

two orders of magnitude, all combine to show that physical adsorption of carbon monoxide in this range is of minor importance, and that the larger part of the total adsorption must consist of gas held in an activated form. The rate of this activated adsorption is very rapid even at -78.5° ; in fact there is considerable evidence, which will not be detailed here, to show that this type of adsorption occurs rapidly even at -183° . The slow sorption first noted at 0° and above is obviously a third kind of process. It may be provisionally regarded as solution, although the possibility that it represents a second type of activated adsorption, sharply distinguishable from the type discussed above, is an attractive alternative.

Although the different types of sorption of carbon monoxide are less sharply separated than in the case of hydrogen, consideration of all the available data permits an approximate estimate of the separate amounts

of gas taken up in each of the three ways. The values thus obtained are shown in Fig. 6, which represents the 300 mm. isobars for physical adsorption (Curve 2), for activated adsorption (Curve 3), and for the observed "solution" (Curve 4). Curve 1, which is the sum of Curves 2, 3 and 4, gives the total observed sorptions.

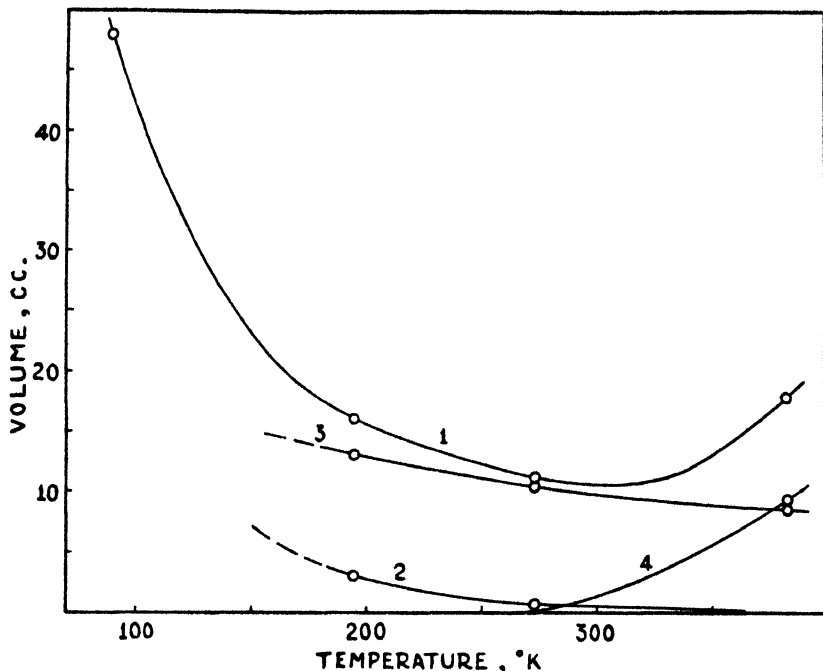


Fig. 6.—Isobars for Carbon Monoxide on Copper at 300 mm. Curve 1: Total Sorption, Curve 2: Physical Adsorption, Curve 3: Activated Adsorption, Curve 4: Solution.

Sorption by Iron.

The following summarised results were obtained with a 54.6 g. sample of iron which was prepared by reduction of fused ferro-ferric oxide (0.15 per cent. aluminium oxide) with hydrogen at 425-450°. The experiments were carried out by Dr. T. A. White, with the collaboration of the author.

Nitrogen.—The isothermal adsorption of nitrogen is shown in Fig. 7, Curves 1, 2, 3, 4. In all cases the rate was apparently instantaneous, except at -191.5° where a few minutes were required to reach equilibrium. These results indicate that physical adsorption is the only process involved at temperatures up to 0° . The following heats of adsorption were obtained from Curves 1 and 2.

Volume adsorbed	:	:	:	8.0	10.0	12.0
Heat of adsorption	:	:	:	3700	2340	2050

At higher temperatures, however, the sorption is greater than at 0° . This is shown by the data given in Table II., which were obtained successively at the temperatures shown, with a given amount of gas in the system.

Little, if any, of the gas taken up at high temperatures is evolved on cooling to 0° . While no definite evidence has been obtained, it is probable that the high-temperature process is activated adsorption, especially

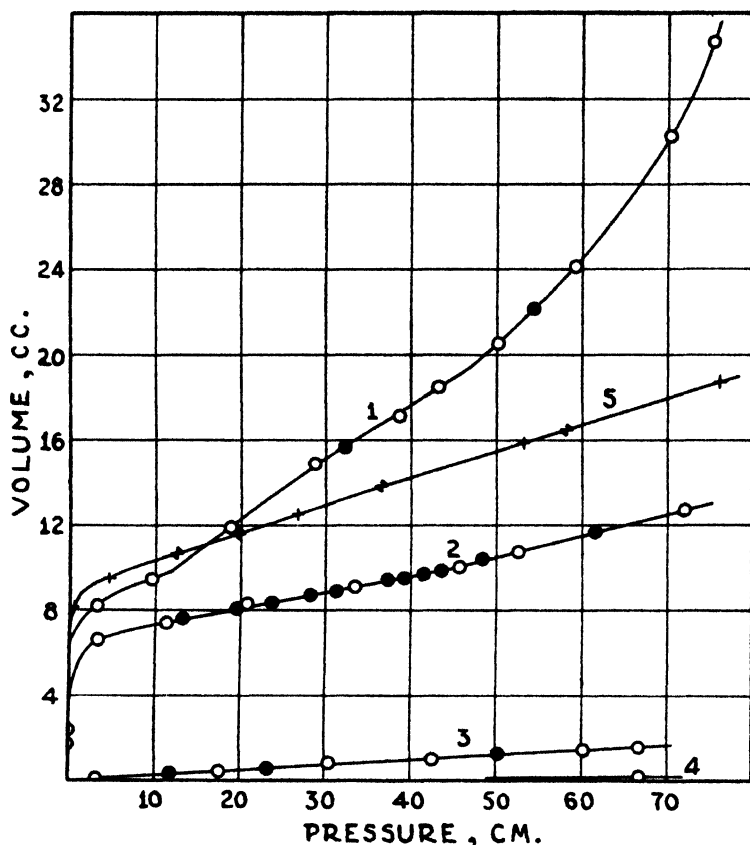


FIG. 7.—Isotherms for Iron. Curves 1, 2, 3, 4 are for Nitrogen at -191.5° , -183° , -78.5° , and 0° , respectively. Curve 5 is for Carbon Monoxide at -183° .

TABLE II.

Temp. ($^{\circ}$ C.).	Pressure (mm.).	Sorption (c.c.).
321	418.0	0.43
0	195.1	0.42
344	425.1	0.54
360	435.6	0.56
408	469.6	0.54
0	195.1	0.42

ally since there is no indication in the literature that gaseous nitrogen dissolves in α -iron.

Carbon Monoxide.—The adsorption of carbon monoxide at -183° is shown in Curve 5 of Fig. 7. The CO : N_2 ratio at this temperature is

1.44 ± 0.02 throughout the entire range of pressure. This fact, together with the apparently instantaneous rate, indicates that here also the process is solely physical adsorption.

At -78.5° there occurs a rapid adsorption of carbon monoxide, followed by a slow process. At 0° the rapid adsorption has nearly disappeared, and the slow process has increased greatly in rate. The rapid process is probably physical adsorption, but the nature of the slow process has not been ascertained.

Hydrogen.—The adsorptions of hydrogen at -195° and -183° are shown in Fig. 8, Curves 1 and 2. The general shape of these isotherms, coupled with the fact that the rates were apparently instant-

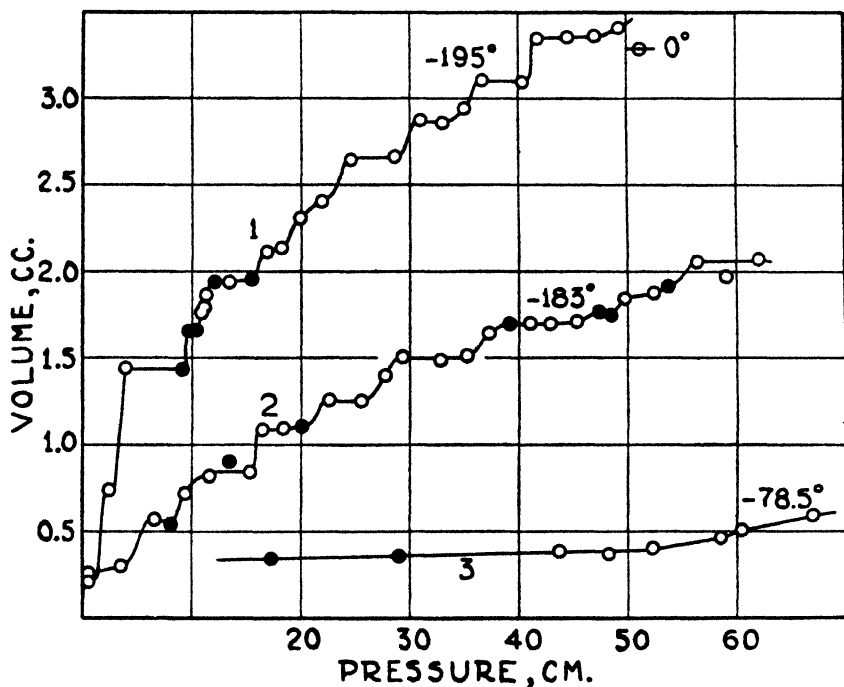


FIG. 8.—Isotherms for Hydrogen on Iron.

aneous, shows that the process involved is physical adsorption. The heat of adsorption obtained from these curves is about 1600 cal.

Curve 3 shows an isotherm for -78.5° . The rates observed here are illuminating. The first two portions of gas admitted to the iron came to equilibrium immediately at pressures of 50 and 258 mm., respectively, but the adsorption in each case was less than 0.05 c.c. The next portion gave an immediate adsorption of 0.30 c.c. at 715 mm. Some gas was then withdrawn, and the adsorption at once decreased to 0.05 c.c. at 405 mm. However, unlike the previous points, this pressure did not remain constant, but slowly decreased until an adsorption of 0.28 c.c. was attained after 16 hours. From this point on, the values shown in Curve 3 were successively obtained, immediate equilibrium being reached in every case. A repetition of this experiment gave practically identical results.

The point of view here adopted furnishes a simple interpretation of

this behaviour. There is a very small and readily reversible physical adsorption at -78.5° , which exhibits steps similar to those at lower temperatures, but here the first step occurs at a pressure of about 600 mm. At one point in the course of following this isotherm, a slow activated adsorption took place to the extent of about 0.3 c.c. The isotherm subsequently obtained has the same form as the original one, but all the values are greater by the 0.3 c.c. adsorbed in the activated form.

At 0° an adsorption of 0.2 to 0.3 c.c. occurred rapidly, but a slow process ensued which had not come to equilibrium in thirty-five days. The value obtained at the end of this time, 3.28 c.c. at 513 mm., is indicated in Fig. 8. At this point the temperature was changed quickly to 110° . The result was an immediate decrease of the sorption to 2.06 c.c. (at 768 mm.). This value did not remain constant, however, but gradually increased during three days to 2.47 c.c. (at 748 mm.), without any sign of an approach to equilibrium.

These experiments prove that at 110° the sorption consists of two different processes, neither of which can be physical adsorption. Measurements carried out wholly at 110° gave the same result, namely, that an initial, rapid process is followed by a second, much slower process. At 210° there is again a rapid process, in which less gas is taken up than at 110° , and the slow process is still apparent. It is probable that the two processes thus distinguished represent activated adsorption and solution. On this basis the activated adsorption is very slow at 0° , but rapidly increases in rate at higher temperatures. The final equilibrium, however, shows a decreasing activated adsorption with increasing temperature. As to the "solution" process first noted at 110° , all that can definitely be said is that after long times of observation there is less solution at 210° than at 110° .

A curious feature of what has been described as activated adsorption is that the rate is *autocatalytic*. At 0° , after the first 0.2 to 0.3 c.c. had been rapidly adsorbed, an induction period of eight to ten hours occurred, during which there was almost no further sorption. Subsequently the rate increased, passed through a maximum, and then decreased. At 110° , in spite of the rapid rate of this process, there was evidence of a similar behaviour. While an autocatalytic rate suggests the possibility that a new phase of iron hydride is formed, this is by no means a necessary conclusion. The data here presented are incapable of distinguishing absolutely between compound formation and activated adsorption, but the interpretation of the results as a whole is simpler in terms of the latter process.

Sorption of Hydrogen by Nickel.

The relatively large adsorptions of hydrogen by nickel at temperatures above -110° , as observed by Benton and White,⁴ have been attributed to solubility by Steacie.⁹ While the course of the isotherms and isobars is strong evidence against this view, the rates of sorption at different temperatures (which were not given in detail by Benton and White) furnish important additional evidence. At -78.5° equilibrium was reached almost immediately. At 0° and higher temperatures, nearly the entire adsorption occurred instantaneously, but a very slow drift ensued, which was obviously a different process from the rapid activated adsorption. Of the observed total sorption of about 7 c.c., approximately 1.1 c.c. at 0° , and 1.6 c.c. at 110° , are accounted for by the slow process,

which had probably not reached equilibrium after the four to five hours of observation. This slow process cannot be the final part of the activated adsorption, since the latter was rapid even at -78.5° . It is doubtless to be ascribed to solution. When solubility is allowed for, however, activated adsorption remains as the major process involved at these temperatures.

Sorption of Oxygen by Silver.

As part of a study of the kinetics of the hydrogen-oxygen combination at silver surfaces, it was shown¹² that considerable quantities of oxygen are taken up by reduced silver in the temperature range, 25 to 110° , and are not given off again in a vacuum at an appreciable rate. The major fraction of the sorption occurred fairly rapidly, but the rate decreased continuously with time, and equilibrium was not reached even after many hours. Since oxygen at atmospheric pressure had never been observed to react with silver at any temperature, it was assumed that the gas was held by activated adsorption.

This system has recently been re-investigated by Mr. L. C. Drake and the author, with unexpected results. At temperatures of $174-200^{\circ}$, it is found that after each addition of oxygen to the system, the pressure slowly decreases for many days, but ultimately approaches a definite value which is *independent of the amount of gas previously taken up*. When gas is withdrawn, the pressure slowly increases and gradually approaches the same value as before. We are obviously dealing here with the formation and decomposition of a definite solid phase of silver oxide. The dissociation pressures thus obtained are in good agreement with values calculated by extrapolation of earlier data at higher temperatures.¹³

At pressures below the dissociation pressure at a given temperature, where oxide formation is impossible, a considerable sorption of oxygen occurs. The major portion of the gas is taken up very rapidly, but this is followed by a slow process which does not come to equilibrium even after many hours. These facts suggest that two different processes are occurring. That such is the case is conclusively shown by the following experiment. A sorption of 7.37 c.c. was observed after twenty-one hours at 158° , the pressure being kept always below the dissociation pressure of the oxide. On rapidly heating the system to 198° , the sorption gradually *decreased* to 6.86 c.c., after which a slow resorption occurred. It may be added that at -78.5° there was a relatively small adsorption, which was rapid and reversible, and clearly of the physical type. In spite of the complication introduced by compound formation, the system, silver-oxygen, is found to exhibit the three processes already distinguished, namely, physical adsorption, activated adsorption, and solution.

Discussion.

The results outlined above show that "sorption" consists in numerous cases of three definitely distinguishable processes. It is impossible to give any simple rule by which the nature of the sorption under any given conditions can be identified with certainty. Rate alone is not a valid criterion, since a slow process may involve activated adsorption, solution,

¹² Benton and Elgin, *J. Am. Chem. Soc.*, **48**, 3027, 1926; **51**, 7, 1929.

¹³ Lewis, *J. Am. Chem. Soc.*, **28**, 139, 1906; Keyes and Hara, *ibid.*, **44**, 479, 1922.

or compound formation, or any combination of these. However, when a particular system is examined over a wide range of temperature, with attention to equilibria as well as rates, it is found that the separate processes can usually be identified and quantitatively estimated. It appears that most of the data in the literature on activated adsorption will have to be re-investigated from this standpoint before definite conclusions can be drawn from them. The information now available, however, is sufficient to provide the following characterisation of the several processes.

Physical Adsorption.—Physical, or non-selective, adsorption is a phenomenon common to all gas-solid systems. Equilibrium is reached with great rapidity. The extent to which different gases are held in this form on a given adsorbent depends primarily on the magnitude of the van der Waals' forces, as measured by the boiling-points or critical temperatures. The adsorption decreases uniformly with increasing temperature, corresponding to a heat of adsorption which is of the order of 2 to 4 times the latent heat of vaporisation. At a temperature 200° above the boiling-point this type of adsorption has become inappreciable, except in those cases like charcoal and silica gel where there is an extraordinary extension of surface. Since the forces involved are not those between two like molecules of gas, but rather those existing between a gaseous molecule and the solid surface, some specificity of different surfaces would be anticipated. Solids with the most intense surface fields of force, as indicated by high melting-points and related properties, should exhibit the largest physical adsorptions per unit area. While the large adsorptions by charcoal and silica may be due in part to this cause, there is considerable evidence that for adsorbents in general extension of surface is the important factor, and that the specific nature of the surface plays at most a minor rôle. Thus the heats of physical adsorption given above for hydrogen and nitrogen on copper and iron do not differ greatly from the corresponding values which have been observed for charcoal, SiO_2 , SnO_2 and similar adsorbents. Furthermore, we have found that copper and nickel surfaces which have been largely covered with hydrogen in the activated form show nearly as great a physical adsorption as the bare surfaces. Here the extension of the surfaces has remained the same, but their nature has been completely altered.

Physical adsorption appears to be characterised by a discontinuous increase of adsorption with pressure. A theory of this phenomenon has been given in detail elsewhere,¹⁴ and cannot be included here. It should be pointed out that our failure to obtain definite evidence of such discontinuities in the large adsorptions of nitrogen and carbon monoxide at the lowest temperatures is doubtless attributable to the fact that too few points were taken on these isotherms. However, the latter are not smooth curves within the experimental error, but exhibit in each case one or two points at which the direction of the isotherm alters more or less sharply. Evidence based on the volume relations at consecutive "breaks," which cannot be detailed here, leads to the view that such breaks represent the completion of successive *layers* of physically adsorbed molecules.

Activated Adsorption.—The occurrence of activated adsorption bears no relation to the physical properties of the absorbent or adsorbate,

¹⁴ Benton and White, *J. Am. Chem. Soc.*, **53**, 3301, 1931.

but is determined by specific interactions of the type characteristic of ordinary chemical reactions. As with the latter, the rate varies widely from case to case, and shows a rapid increase with temperature. The rates are much slower on adsorbents which have been "deactivated" by heat treatment or poisons. The heats of adsorption also differ greatly, but are much larger than for physical adsorption.

We believe with Langmuir that the only essential difference between activated adsorption and the formation of an ordinary chemical compound is that in the former case, the atoms in the surface of the adsorbent remain as part of the crystal lattice, and no new *phase* is produced. On this view it is easy to understand the frequent observation that the heat of activated adsorption greatly exceeds the heat of formation of the definite compound. In such cases the change from activated adsorption to definite compound would be *endothermic*, so that at not too elevated temperatures activated adsorption may well represent the more stable system thermodynamically. In a number of systems large activated adsorptions have in fact been observed under conditions where compound formation is impossible. In addition to the case of oxygen-silver already referred to, further examples are found in the systems, oxygen-gold,¹⁵ and nickel-carbon monoxide.¹⁶ While little is known about the equilibria, it is probable that copper, iron, and nickel in contact with hydrogen are additional examples. When conditions permit both activated adsorption and compound formation, the former process is much more rapid than the latter. The evidence available points strongly to the conclusion³ that activated adsorption is a necessary intermediate stage in compound formation, and that the rate of conversion of the former into the latter is the slow, rate-determining step, at least at moderate temperatures.

Solution.—It is possible that some of the phenomena which have been described as "solubility" really represent a second type of activated adsorption. On the other hand, it was shown by Griffin¹⁷ in this laboratory that small quantities of carbon monoxide slightly increase the adsorption of hydrogen by copper at low pressures, but markedly *decrease* the sorption at higher pressures, and these results were given a simple interpretation on the assumption that unpoisoned copper is capable of dissolving considerable quantities of hydrogen at ordinary temperatures, but this solubility is inhibited when the most active spots are occupied by carbon monoxide. Similar results were observed for nickel,¹⁸ although the apparent solubilities were smaller in this case. Pending definite identification of more than a single type of activated adsorption, it seems best to postulate the well-recognised process of solution. Unfortunately, reliable conclusions cannot be drawn from our measurements regarding the variation of such solubility with temperature and pressure, since final equilibrium was seldom, if ever, attained.

In no case examined does solubility make its appearance until temperatures are reached at which there is a pronounced activated adsorption. While conceivably fortuitous, this fact suggests the possibility that activated adsorption is a necessary precedent to solution. Our extensive data on rates of solution, and their bearing on this question, cannot be adequately discussed in this place.

¹⁵ Benton and Elgin, *J. Am. Chem. Soc.*, **49**, 2426, 1927.

¹⁶ Taylor and Burns, *ibid.*, **43**, 1273, 1921.

¹⁷ Griffin, *J. Am. Chem. Soc.*, **49**, 2136, 1927.

¹⁸ White and Benton, *J. Physic. Chem.*, **35**, 1784, 1931.

Summary.

Following a review of the development of the idea of activated adsorption, new investigations of the following systems are described: Cu — N₂, Cu — H₂, Cu — CO, Fe — N₂, Fe — CO, Fe — H₂, Ni — H₂, Ag — O₂.

From experiments on both equilibria and rates over a wide range of temperature, and particularly from the effects observed following rapid changes of temperature, definite evidence has been obtained in all cases except those involving nitrogen, that three different processes occur, namely, physical adsorption, activated adsorption, and a third process which is probably solubility. The contribution of each of these processes to the total sorption has been determined.

On the basis of the results obtained and other data in the literature, the principal characteristics of the different processes have been outlined. The importance of activated adsorption as an intermediate stage in the formation of definite chemical compounds and in solubility is briefly summarised.

*Cobb Chemical Laboratory,
University, Virginia.*

DISCONTINUITIES IN ADSORPTION PROCESSES.

BY A. J. ALLMAND, L. J. BURRAGE AND R. CHAPLIN.

(Received 12th December, 1931.)

About six years ago, workers in this laboratory first began to obtain evidence to the effect that the process of the adsorption of vapours on charcoal might be discontinuous in nature. The results were, for some considerable time, regarded with not unnatural suspicion, and every attempt was made to eliminate the errors to which they might be due. Such attempts were unsuccessful, and the real existence of these discontinuous phenomena is now regarded by us as proven. What follows is merely a summary of the evidence on which this conclusion is based.

1. Synopsis of Results already Published.

(a) **Experiments at Low Pressures of Vapour and in Absence of Air.**—The first observed discontinuities were noticed during these measurements, limited by the experimental method (use of the Pirani gauge) to maximum pressures of the order of 0.2–0.5 mm. They appeared in the isosteres of all CCl₄—charcoal systems, determined over temperature ranges varying between 0°–90°, whenever the CCl₄ pressure exceeded about 0.1 mm., the molecular heat of adsorption, constant up to that pressure, undergoing a sudden diminution.¹ They were also observed at the same pressure in certain isothermals² measured at 25°, and indications were obtained of the existence of further breaks at higher pressures. The nature of these isothermal breaks is expressed by saying

¹ Allmand and Chaplin, *Proc. Roy. Soc.* **129A**, 257, 1930.

² Allmand and Chaplin, *loc. cit.*, p. 246; Allmand and Puttick, *ibid.*, **130**, 197, 1930.

that, as the pressure is increased and reaches a certain figure, the value of dq/dp abruptly increases, then decreasing continuously until the next discontinuity is reached. The general effect is to cause the appearance on the isothermal of sharply defined loops, concave to the pressure axis. Further work³ showed that the isosteres for CS_2 on a whole series of charcoals, determined over the same temperature range, also exhibited discontinuities at pressures of 0.1 mm. or a little higher. One carefully studied isothermal showed the same phenomenon.

(b) Experiments in Presence of Air, using the Retentivity Technique.—This method of obtaining approximate sorption isothermals, originally devised by Allmand, Manning and Burrage,⁴ was developed later by Burrage⁵ in such a way as to furnish true isothermals. A very large number of such isothermals have been measured⁶ on a variety of charcoals, chiefly using water vapour or CCl_4 as sorbates, and working either at 100° or at 25°. The invariable result has been a curve of markedly discontinuous structure, showing a first break at about 0.1 mm., independent of the nature of both charcoal and sorbate, and also of temperature, and showing, in addition, a large number of similar breaks at higher pressures, some of them well, some indistinctly, marked. Attempts to correlate satisfactorily either the pressure values at which breaks occurred, or the increments of sorbate between adjacent breaks, led to no particular success, although there was evidence of a certain degree of regularity in the pressure values.

(c) Experiments at Moderate Pressures of Vapour and in Absence of Air.—These measurements⁷ were undertaken primarily to confirm the general nature of the results just described, obtained, as they were, by a new and untried technique, and also to provide a rather greater variety of experimental material. Apparatus and sorbent were thoroughly degassed before admission of the vapour, and equilibrium pressures were read off by a mercury manometer, taking measures to avoid false pressures due to displaced gases, and making readings at narrow pressure intervals in order better to define the anticipated breaks. As a result, it was found that every charcoal isothermal investigated, using as sorbates CCl_4 , CS_2 , C_6H_6 , H_2O , $n\text{-C}_5\text{H}_{11}\text{OH}$ and CO_2 (the latter above and below its critical temperature), exhibited breaks. In two cases of CCl_4 isothermals, it could be shown that the broken curves were reversible in nature.

(d) Experiments with Silica Gel.—Isothermals⁸ over a limited pressure range, determined by the approximate retentivity method, showed a very markedly discontinuous and step-like structure in the case of water vapour, and definite evidence of minor discontinuities with CCl_4 . On the other hand, a benzene isothermal determined in absence of air appeared continuous within experimental error between 7.5–12 mm.

2. New Results.

(e) Carbon Dioxide on Charcoal.—The results mentioned under 1(c) as having been obtained with CO_2 and charcoal were known not to represent equilibrium data, and would have been doubted if they had

³ Allmand and Lizius, *Proc. Roy. Soc.*, **134A**, 554, 1932.

⁴ *J. Soc. Chem. Ind.*, **47**, 369 T, 372 T, 1928.

⁵ *J. Physic. Chem.*, **34**, 2202, 1930.

⁶ Allmand and Burrage, *J. Physic. Chem.*, **35**, 1692, 1931.

⁷ Allmand and Puttick, *loc. cit.*; Allmand and Burrage, *Proc. Roy. Soc.*, **130A**, 610, 1931.

stood alone. In addition to this, a CO_2 -charcoal system is of rather particular interest, in view of the special rôle played by the slow displacement of this gas from a charcoal surface during adsorption measurements with other substances. Also a further test of the reproducibility of the breaks was thought desirable. Consequently, an isothermal has been examined⁸ in great detail by the static method, about 350 points having been determined at 25° within the pressure range $81 - 0.04$ mm., viz., 192 points covering the range $81 - 1.55$ mm. (series I), then 37 points between $1.78 - 0.04$ mm. (series II), followed by 90 points covering $16.80 - 1.60$ mm. (series III), and finally 28 points ranging between 79.4 and 12.75 mm. (series IV). A complex discontinuous isothermal

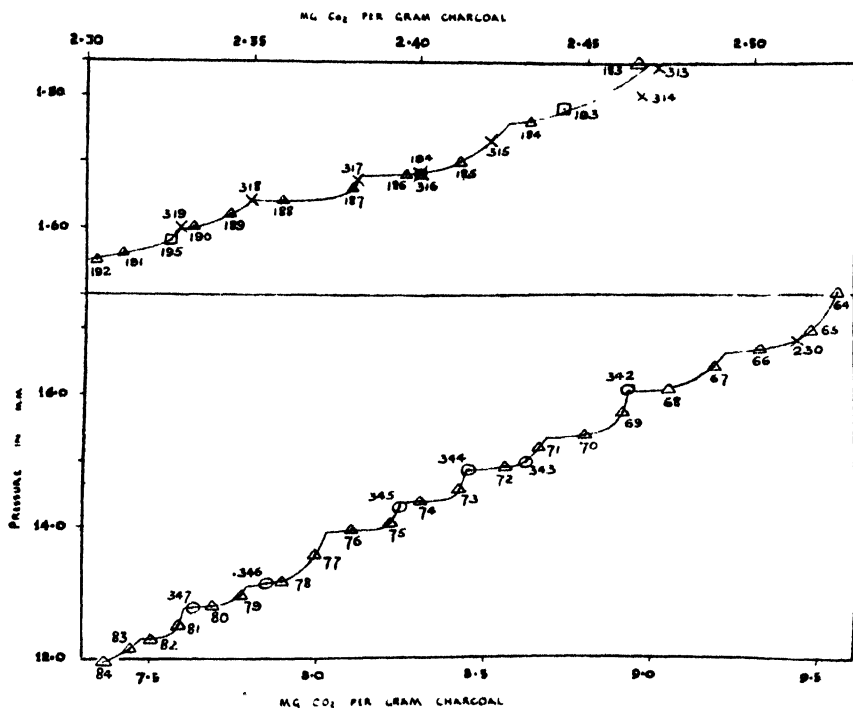


FIG. 1.

was obtained over the whole pressure range and, moreover, the different desorption curves were superposable in detail when their pressure ranges overlapped. Fig. 1 contains plotted data for the pressure intervals $1.55 - 1.85$ mm. and $12.0 - 17.5$ mm., involving respectively points determined during series I, II, III and I, III, IV. (I Δ ; II \square ; III \times ; IV \odot .)

(f) **Various Vapours on Charcoal and on Silica Gel, Employing an Improved Retentivity Technique.**—These experiments⁹ have furnished the very striking result that, in every case investigated, both with charcoals, activated and unactivated, and also with silica gel, the isothermals above 0.1 mm. appear to consist of sharply defined rectangular steps, with the treads, as drawn, parallel to the q axis. (Five different charcoals, and H_2O , CH_3OH , CCl_4 and SO_2 have been worked with.)

^{8, 9} Burrage—unpublished work.

Such a structure had already been noticed with water and silica gel—see 1(d),—and the fact that, with a more precise method of measurement, it is now generally obtained, is ascribed to the very effective displacement of residual gases and vapours brought about by the method of charging with the vapour under experiment. In the case of charcoals, it is the residual oxygen charge which is thus removed. It may be added that *sorption* isothermals, determined by charging in an air stream, also show a step-like structure.

One further important point has emerged, *viz.* that, using CCl_4 at 25° , the quantity increments between successive breaks (given by the "treads" of the "steps") are practically constant within the experimental error, both with charcoal and with silica gel, over the whole pressure range covered in the experiments, *viz.* 8—0.1 mm. (See Fig. 2.) On the other hand, with water vapour, whilst these decrements are con-

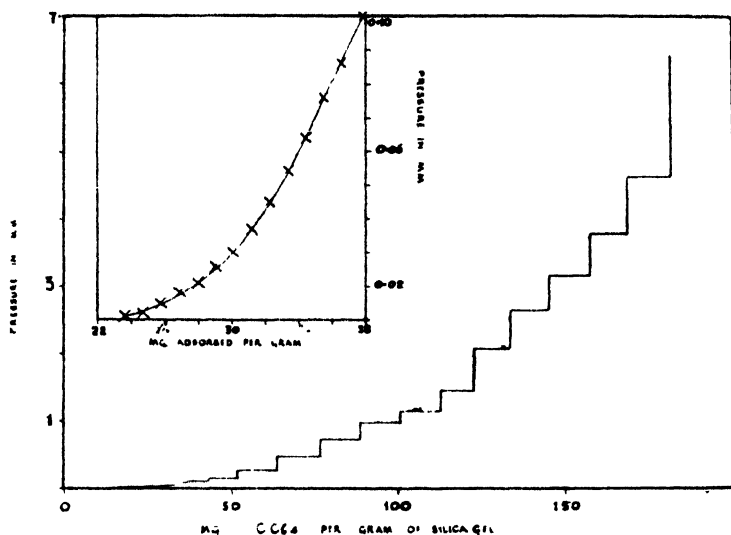


FIG. 2.

stant when starting at high pressures, they increase at intermediate pressures and finally fall off again as the pressure is progressively reduced. It is of interest to note that the absence of discontinuities below 0.1 mm. (provided that disturbing influences are not present) found in the earlier experiments, is confirmed.

(g) **Adsorption of Mixtures of Vapours on Charcoal.**—Experiments using the Pirani gauge low pressure technique¹⁰ have shown that the adsorption of mixtures of the vapours of CS_2 and H_2O by charcoals also may involve discontinuities. The work is difficult, and the relations are not too exactly defined. But it can be stated that the isothermals of CS_2 on charcoals holding a constant charge of water show signs of discontinuities, and this is very decidedly the case when the effect of a variation in the water charge on the equilibrium CS_2 pressures exerted by a constant charge of CS_2 at constant temperature is considered; the $p_{\text{CS}_2}/q_{\text{H}_2\text{O}}$ curves sometimes show very marked breaks.

¹⁰ Allmand and Lizius—*unpublished work*.

(h) **Adsorption from Solution.**—Experiments¹¹ have been carried out on the adsorption of phenol from aqueous solution by an activated charcoal. The isothermals, both at 25° and at 60°, are of a marked step-like character, and are reversible, or very nearly so.

3. Other Similar Results.

A summary, up to the end of 1930, of observations from other laboratories indicating that adsorption processes may be discontinuous in nature, has been given elsewhere.¹² Since that date has appeared an important paper by Benton and White,¹³ in which are given details of discontinuous hydrogen isothermals measured on reduced nickel, copper and iron catalysts, both bare and poisoned with CO, together with similar nitrogen isothermals on copper and iron. These authors in addition have put forward a theory which accounts very plausibly for a large number of the facts observed by them, and which has points in common with certain views which we held a few years back,¹⁴ but which we have not been able to develop to our satisfaction in the interval, owing to the complexity of the available experimental data, and the wish to elucidate them more exactly. The analysis of the new results communicated in this paper is not completed, and fresh data are accumulating; on that account we shall not attempt here to elaborate further our preliminary views as already put forward¹⁵.

*University of London,
King's College.*

¹¹ Chaplin (work carried out in the Research Laboratories of the Gas, Light, and Coke Company), *in course of publication*.

¹² Allmand and Burrage, *Proc. Roy. Soc.*, **130A**, 626, 1931.

¹³ *J. Amer. Chem. Soc.*, **53**, 3301, 1931.

¹⁴ The following is an extract from the printed report of a paper read by one of us in Oxford in December, 1929:—

The speaker finally briefly discussed possible explanations for the discontinuous structure of these isothermals which his experiments seemed to make probable. As a working hypothesis only (for there are difficulties and objections to be overcome and far more experimental work is needed) he inclined to the following. Adsorption on charcoal starts out from "active centres," from which "islands" of sorbate spread out, in the sense of Polanyi and Goldmann. An "island" is actually composed of a series of concentric rings. The completion of a ring and the commencement of a new one is marked by a "break." The spatial position of the rings with respect to the active centres is not invariable—they are closer in at high temperatures and with low-boiling sorbates than at low temperatures or with high-boiling sorbates. So Polanyi's "constant potential surfaces" (or lines) have no connection with the breaks.

¹⁵ See preceding footnote; also Allmand and Burrage, *loc. cit.*, pp. 627 *et seq.*

A POSSIBLE CONNECTION BETWEEN ACTIVATED ADSORPTION AND GAS DISPLACEMENT EFFECTS.

BY A. J. ALLMAND AND R. CHAPLIN.

Received 26th January, 1932.

Taylor¹ has recently drawn attention to certain facts concerning the effects of temperature on the kinetics of the adsorption of gases by solids and on the quantities of such gases taken up, which indicate that the process of adsorption can sometimes require an energy of activation, that the gas thus adsorbed is frequently thereby rendered chemically active, and that the heats of adsorption involved are considerably greater than those found for unactivated adsorption of the same gas by the same surface. The evidence for the existence of some such process is indeed very strong, and the point arises as to its exact nature, if indeed the latter is always the same.

Taylor himself is inclined to lay the emphasis on the difference between adsorption involving van der Waals' forces and that involving non-classical interchange energies between sorbent and sorbate—or, briefly, between "physical" and "chemical" adsorption. The former is unactivated, and the latter, in which the binding between sorbent and sorbate is quite similar to that involved in the Heitler-London homo-polar valence forces, is activated adsorption. Whilst such adsorptive binding would certainly require activation energy (examples are probably furnished by oxygen and hydrogen on charcoal) it seems that the adsorbed molecules or chemi-adsorptive compounds would be immobile, or relatively so, on the surface (Rideal),² and such "irreversibly adsorbed" molecules (Garner) would not be chemically reactive (Bonhoeffer and Farkas; Garner). According to Ward, on the other hand, the activation involved is one of a diffusion process into the interior of the solid, either through the lattice or along grain boundaries or Smekal cracks. That diffusion of adsorbate on the external surface of a sorbent can require activation energy would appear proved from the work of Volmer and of Becker. Rideal quotes less direct evidence for similar diffusion into the internal surface of a solid (as also into the lattice) and the process in general is considered in the papers of Chariton *et al.*, Garner, and Lennard-Jones.

During the course of the discussion, the suggestion was made that, at all events in some cases of adsorption, the process requiring activation may be the displacement of residual gas from the adsorbing surface by the adsorbed molecules, and it is this suggestion which is now elaborated. Our primary reasons for putting it forward are the results obtained in this laboratory whilst studying the adsorption of CO₂ and of various vapours by charcoal.³ A summary of the conclusions drawn from our

¹ *J. Amer. Chem. Soc.*, **53**, 578, 1931.

² When an author's name is quoted without further detail, the reference is to the paper contributed by him to the present General Discussion.

³ (I.) *Proc. Roy. Soc.*, **129A**, 235, 252, 1930; (II.) *Ibid.*, **130**, 197, 1930; (III.) *Ibid.*, **130**, 210, 1930; (IV.) *Ibid.*, **130**, 610, 1931; (V.) *Ibid.*, **132**, 460, 1931; (VI.) *Ibid.*, **134**, 554, 1932.

experiments up to a point is given in (I.) pp. 261 *et seq.*; further work has led to additions, rather than to modifications. Briefly, these conclusions are as follows.

Adsorption of a gas or vapour on charcoal is accompanied by displacement of oxides of carbon from the charcoal surface, where these gases are held by forces which vary very much in intensity from point to point. Consequently, whilst some of the gas is readily displaced, some of it comes off with much difficulty. The frequently observed slow rate of adsorption ("drift") is due to the necessity of displacing these tightly held gases, which are the same as those removed with even more difficulty by prolonged high temperature evacuation. It is *not* due to slow diffusion of vapour to difficultly accessible areas or pores in the interior of the charcoal (II.). Chemically activated charcoals have their "active centres" occupied by mineral matter; consequently they do not bind much oxygen, not much gas is given off when they adsorb vapours, equilibrium is rapid and reversible, and the type of isothermal at low pressures differs correspondingly (V.). The process of the elimination of these gases can be split up into two stages, the breaking up of the carbon-oxygen surface complex (to use a non-committal term) with formation of ordinarily adsorbed CO_2 or CO, and the actual displacement from the charcoal of these adsorbed oxides. The former of these two processes is the one which determines the rate of drift (VI.), and the removal of a small quantity of such tightly bound gas has a relatively large effect on the quantity of vapour sorbed.⁴ The most effective way of removing this tightly bound oxygen is by a stream of vapour, even if air-borne (Allmand, Burrage, and Chaplin).

The retarding effect on the setting-up of adsorption equilibrium exerted by small quantities of foreign gases has been noted by many other observers (Harned,⁵ McGavack and Patrick,⁶ Davidheiser and Patrick,⁷ Coolidge,⁸ Gregg,⁹ McBain *et al.*,¹⁰ Maxted,¹¹ Benton). The detailed results of Harned and of Coolidge are particularly suggestive. Patrick¹² has shown that vapour may be adsorbed from an air-borne stream without the air causing any complication.

There are a few points we should like to mention in extension of the above. Firstly, we think that the displacement of the oxygen (as oxides of carbon) is chiefly effected, not by molecules of sorbent present in the gas phase, but by such molecules as are already adsorbed; these gradually occupy the favoured positions in possession of the CO_2 and CO units of the carbon-oxygen complex whilst the latter are in course of executing occasional vibrations of particularly high amplitude. Secondly, we think that the effect of a gas stream in rapidly clearing up the charcoal surface is best explained on the assumption that the liberated CO and CO_2 , unless thus removed, can in their turn be re-adsorbed in the high potential "seatings" which their displacement has produced in the charcoal surface. Lowry and Hulett quote evidence to this effect.¹³

Lastly, some unpublished experiments of Shiels¹⁴ are of interest, as

⁴ Similar observations have been made by others.

⁵ *J. Amer. Chem. Soc.*, **42**, 372, 1920.

⁶ *Ibid.*, **42**, 946, 1920.

⁷ *Ibid.*, **46**, 596, 1924.

⁸ *J. Phys. Chem.*, **34**, 1439, 1930.

⁹ *Koll. Zeitsch.* (Zsigmondy Erg. Bd.), **36**, 272, 1925.

¹⁰ *J. Amer. Chem. Soc.*, **42**, 1417, 1920.

¹¹ *Thesis* (London), 1923.

¹² *Ibid.*, **44**, 1, 1922.

¹³ *J. Chem. Soc.*, **1927**, 1494.

¹⁴ *J. Chem. Soc.*, **1931**, 2203.

giving an indication of the order of the activation energy involved in slow adsorption, if our contention, that this activation energy is required in order to displace from the charcoal the *same* gases that are removed by high temperature degassing, is correct. (We have available at the moment no actual comparative measurements of adsorption velocities at different temperatures.) Shiels degassed charcoal specimens at definite high temperatures, cooled down to room temperature, shut off the pumps, raised the temperature continuously, and read off the observed gas pressures by means of a McLeod gauge at intervals of a few minutes. The data obtained were plotted as $\log p/T^{-1}$, and the slope of a graph gives a value (Q) which will be somewhere intermediate between the energy absorbed in desorption and the sum of this energy and the activation energy of desorption (if any). The results, for which no particular accuracy is claimed, were as follows:—

1. Charcoal degassed at 250°. Graph linear (eight points) up to 190° C., with $Q = 3.4$ Cals.; then a sudden break, and another linear section up to 270° C., with $Q = 30.6$ Cals.

2. Charcoal degassed at 250°. Four points only. Q about 1.5 Cals. between 170°–200°, and 41.1 Cals. between 260°–280°.

3. Charcoal degassed at 500°. Linear graph (five points) between 500° and 600° C., with $Q = 54.9$ Cals. Specimen cooled to room temperature and reheated. Four observations only. $Q = 23.8$ Cals. between 440°–480°, and 51.2 Cals. between 535°–610° C.

In the course of many evacuation experiments carried out on charcoal systems, Shiels noted a rush of gas at 250°–270°, and at second one at about 600°. Analysis of these gases showed CO_2 and CO to predominate respectively, and it is tempting to ascribe the low figures of 1.5 and 3.4 Cals. to desorption of CO_2 adsorbed in the ordinary way, the figures of 23.8–41.1 Cals. to the expulsion of CO_2 from the carbon-oxygen "complex," and the high values of 54.9 and 51.2 Cals. to a similar expulsion of CO .

The final stages in adsorption processes on charcoal have then several of the characteristics ascribed by Taylor to activated adsorption. As the process which requires this activation energy appears fairly obvious, we are led to suggest that a similar cause may also be operative in, *e.g.*, the cases quoted by Taylor, Benton, Maxted and Hassid, and Frankenburg and Hodler. The difficulty of freeing solid surfaces in general from adsorbed gases is well known, and has been referred to by several contributors to the present symposium. And although it may be objected that the quantities of gas involved would be too small to cause effects of the magnitudes observed, yet such behaviour is precisely what we have noticed when working with charcoals; a minute gas displacement is accompanied by a relatively very large increase in adsorption, and rough calculations show the molecular ratio of adsorption increment to gas displacement to be of the order of $10^4:1$ in certain cases.

Brief reference to the experiments of Frankenburg and Hodler is instructive. To activate their tungsten powder, the surface has to be cleaned from oxygen. The process is a slow one, and it is chiefly the adsorption capacity at low pressures which is thereby increased. On standing *in vacuo*, the activated powder slowly loses its properties; this is ascribed to the surface again taking up traces of oxygen. The specimens actually used were known to contain small quantities of this gas, which were deliberately left in. The adsorptive properties of different specimens towards hydrogen are closely paralleled by their relative

powers of adsorbing other gases and of catalysing ammonia decomposition, *i.e.*, there is an absence of any selective effect. The intermediate temperature regions of the hydrogen isobars, in which adsorption increases with rising temperature ("remarkable and at present inexplicable") are irreversible; if the temperature be lowered, the adsorption now increases. Analogous anomalous phenomena are noted with tungsten-nitrogen systems, and in NH_3 decomposition on the tungsten surface. Taylor's "active patches" are involved. With catalysts less free from oxygen, and therefore less active in every way, the abnormalities become less pronounced.

We submit that a preliminary working hypothesis, which explains satisfactorily all the results so far communicated, is the assumption of a residual oxygen charge on the tungsten surface which is very slowly cleaned up in the course of the experiments, and it appears to us that other cases of activated adsorption may be capable of a similar interpretation. There is, of course, one type of experiment which would be crucial; the results would either definitely disprove the hypothesis in the particular case or else render it highly probable. It does not appear to have been done hitherto. Imagine a specimen of sorbent brought to equilibrium at a fairly high pressure and at a temperature above the region of anomaly, *i.e.*, in a temperature region where activated adsorption takes place readily and the isobar is reversible. Let the gas now be pumped out completely at this temperature, it being assumed that oxygen is rigidly excluded and that no sintering takes place. If necessary, let the whole process be repeated several times. Suppose the sorbent now cooled to a low temperature, at which normally only unactivated adsorption occurs, and fresh gas admitted. If the high temperature treatment has removed adsorbed gases which had previously been active as suggested, then rapid adsorption will take place at this low temperature, to a total extent corresponding to the sum of the previous activated and unactivated adsorptions. If this is not so, then clearly the case must be one to which the conception of Taylor or that of Ward must apply.

A few remarks may be added in conclusion. The slow rate of cathodic over-voltage rise mentioned in the discussion is perhaps due to displacement of oxygen from the surface layers of the cathode by adsorbed H atoms. The fact that Ward finds proportionality between the rate of the assumed activated diffusion and the surface concentration is in accord with our view that displacement is effected by already adsorbed vapour molecules rather than by those in the vapour space. The qualitative distinction between physical and activated adsorption will disappear if our suggestion prove correct, always, of course, excepting those cases of adsorption where the Heitler-London valence forces are operative. And chemical activation will again be ascribable to intense physical adsorption on high potential "active centres," rather than to adsorption of a different, if not new, type.

*University of London,
King's College.*

THE KINETICS OF ADSORPTION IN RELATION TO REACTION VELOCITY.

BY F. HURN CONSTABLE, D.Sc., PH.D.

Received 3rd, December, 1931.

The method of treatment adopted by Langmuir for the dynamics of heterogeneous catalytic reactions enables us to calculate the fraction of a surface that is covered with the reactants and so to develop an expression for the reaction velocity. With the growth of evidence that these surfaces were not uniformly active it appeared that some special method of treatment should be adopted in order that the results obtained could not be open to the question that they had been obtained for uniform surfaces only. In a paper¹ it was shown that in many cases in spite of the heterogeneous nature of the centres on which catalytic reactions take place it was in general difficult from dynamical measurements alone to distinguish that any such heterogeneity existed. The general conclusions were that the first approximation to the distribution of the centres of activity over the surface was an exponential one, and that such surfaces cause decomposition as if they were mostly composed of centres of activity associated with a heat of activation equal to the lowest value in the exponential distribution, in spite of the fact that the number of such centres may be much smaller than those with a higher value of heat of activation. Differences were found between the value of the heat of activation obtained from the temperature coefficient from the heterogeneous reaction, the mean value of the heat of activation averaged over all the reacting molecules, and the mean value of the heat of activation on the surface. These differences, however, were not obvious from results of chemical change measured either by the flow method or by measurements of reaction velocity in closed vessels.

In a further series of papers² a dynamics was developed for these heterogeneous centres in terms of the mean lives of the reacting molecules on the surface. If a surface be unsaturated then any active centre of the surface will not always be occupied by the reactant; at times it will be wholly free from absorbed gas. When the surface approaches saturation it is evident that the fraction of any time interval that the active centre is free from absorbed gas will become smaller and smaller, ultimately vanishing with saturation.

Whatever the mechanism of the surface chemical change between the reacting molecules may be it is necessary that the reacting molecules should be present together, for action at a distance is impossible. The rate of an unimolecular reaction is therefore proportional to the fraction of a given time interval that the active centre is occupied by the reacting substance, it being understood that the active centre may adsorb unreacting substances or may be left completely free from adsorbed molecules. Thus, the probability of an unimolecular reaction at any one

¹ *Proc. Roy. Soc.*, 108A, 355, 1925.

² *Proc. Camb. Phil. Soc.*, 73B, 1925; 172, 1926; 593 and 832, 1927; 56, 291 and 307, 1928.

centre is determined by the fraction of any time interval t that this centre is occupied by molecules capable of reaction. In general if the reaction be n -molecular then the velocity of chemical change is proportional to the products of the fractional time intervals each adjacent centre is occupied by the reacting substances. These intervals may be conveniently called fractional times of occupation. Using this terminology there appears a new law for surface action resembling the law of mass action in homogeneous systems but replacing it. The rate at which the surface reaction proceeds is proportional to the product of the n th powers of the fractional times of occupation of the centres of activity for each reacting species integrated over the whole surface. It is possible by utilising this principle to elucidate the cause of a reaction in which both reactants and resultants are adsorbed.

General Type of Equations Obtained.

(1) Applicable to Flow Methods.

In these cases the reactants are passed over the catalyst at such speed that the concentration of the resultants is negligible. Under these conditions inert diluents usually exert a depressing action on the rate of reaction except where complexes are formed on the surface. If v be the fractional reaction velocity and p the fractional partial pressure of the reactant, then—

$$\frac{1}{v} = (1 - \lambda) + \frac{\lambda}{p}$$

where λ is a constant. The general equation is a product of the type—

$$v = \pi_{p_n} \left(\frac{1}{1 - \lambda_p + \lambda_{p/p_n}} \right).$$

(2) Reaction in Closed Vessels.

When the reaction is bimolecular A and B are the initial concentrations of the reactants and x the amount transformed in time t ; then—

$$kt = Ax + B \log \frac{a}{a-x} + C \log \frac{b}{b-x},$$

where k is a constant independent of t , a , and b . According as the values of the constants A , B , and C are changed any type of combination is possible. The velocity may be initially small, rise to a maximum and die away or it may continuously rise; it may be constant throughout or it may continuously fall. Such types of reaction velocity time curves have been found by direct experiment.

St. Johns, Letchworth.

NEW EXPERIMENTS ON THE MECHANISM OF THE CATALYSIS OF AMMONIA ON TUNGSTEN.*

BY W. FRANKENBURGER AND A. HODLER.

Received in German, 29th December, 1931, and translated by Eric K. Rideal.

In spite of many valuable investigations¹ on the kinetics of the formation and decomposition of ammonia on metallic and oxide contact materials, it has not yet proved possible to disentangle the complex reaction into its components, and thus to prove experimentally by what mechanism involving the contact material the ammonia molecule is built up from or decomposed into molecular nitrogen and hydrogen. It is well known that the measured rates of synthesis or decomposition of ammonia at metallic surfaces are the result of separate individual reactions, and that these partial processes are greatly influenced both by the nature and structure of the catalytic surface. Until now no quantitative data have been obtained for these elementary processes localised on the catalyst surface.

We have attempted by a detailed study of a single example to analyse more sharply the reactive mechanism of the ammonia catalysis at metallic surfaces. Tungsten² proved to be a very suitable metal for this purpose. In order to answer the most important questions, a whole series of separate investigations proved necessary, the chief results of which³ are enumerated shortly in the following pages:—

The measurements were extended to the study of the following phenomena:—

- (1) Preparation of tungsten with reproducible adsorption and catalytic properties ("active" tungsten).
- (2) Behaviour of molecular hydrogen in contact with "active" tungsten.
- (3) Behaviour of molecular nitrogen in contact with "active" tungsten.
- (4) Adsorption of ammonia on "active" tungsten.
- (5) Behaviour of the above gases on *simultaneous* adsorption or reaction with tungsten.
- (6) Decomposition of ammonia on tungsten surfaces with the formation of tungsten nitride or tungsten imide (the first stage in the catalytic decomposition) and the kinetics of this decomposition in the adsorption layers.

* Communication from the research laboratory at Oppau of the I. G., Ludwigshafen, a/Rh.

¹ Ullmann, *Encyclopædia of Technical Chemistry*, 2nd edition, 391, 1928; Literature up to 1928; Winter, *Z. physik. Chem.*, **13B**, 401, 1931; K. Dixon, *J.A.C.S.*, **53**, 1763, 2071, 1931; W. Steiner, *Z. physik. Chem.*, **14B**, 397, 1931; *ibid.*, *Z. Elektrochem.*, **36**, 807, 1930.

² Tungsten was chosen as contact substance on account of its high sintering temperature. This renders possible the attainment of the temperature (750°) necessary for reduction and degassing without any concomitant irreversible alteration of the surface structure, thus retaining its adsorptive and catalytic properties.

³ Many additional data, as well as the apparatus and method of operation, will be given in separate publications.

1. Preparation of a Tungsten with Reproducible Adsorptive and Catalytic Properties ("Active" Tungsten).

Of prime importance in carrying out this work is the preparation and utilisation of a preparation of tungsten possessing a high specific surface and always reproducible in adsorptive and catalytic properties. As raw material tungsten powder⁴ was employed, especially one (C83) of average particle size, 1.86×10^{-4} cm. and with a "macroscopic"⁵ surface of 1700 cm.²/gm.

To ensure the above conditions, this "ordinary" superficially oxidised powder had to have a pretreatment, especially a reduction with the present hydrogen and then an evacuation at a relatively high temperature, 750°. By this operation the surface was cleaned from oxygen, both combined and adsorbed,⁷ which reduces so markedly both the adsorption and catalytic properties of the metal, and the metal in this state in contrast to its former state is "activated," i.e. is brought into a state of higher adsorptive and catalytic activity. The adsorption isotherms in Fig. 1 show the increase in adsorptive power of a powder (C83) for hydrogen with increasing periods of prior reduction.

The degree of activation of a sample of powder can thus be clearly defined by its *power for adsorbing hydrogen* under definite conditions of pressure and temperature. A great number of experiments showed that with its behaviour in adsorbing hydrogen there was a close parallelism in its behaviour in adsorbing other gases as well as in its catalytic activity in the decomposition of ammonia.⁸ Thus, if the hydrogen isotherms of two samples were identical, the powders were found to be equal in every other respect, e.g. the decomposition of ammonia. On the basis of this clear definition, it was now possible to give⁶ a definite and reproducible degree of activation to every sample or apparently poisoned sample of a given preparation.

Powder prepared in this manner ("active") was now employed for

⁴ The powders supplied by the Osram Co. of Berlin were described as (1) Tungsten C83, medium grain size; (2) Tungsten C19, c, medium grain size; (3) Tungsten, C97, medium grain size.

⁵ By "macroscopic" is meant the total surface of the smooth crystalline surfaces of massive particles. The particle size was determined by microphotography of single particles and the surface derived therefrom, taking into consideration a size distribution curve and the assumption of cubic form. The correctness of the size of the macroscopic surface determined in this way is rendered probable by its agreement with the area of the molecular saturation maximum of adsorbed ammonia (see § 4), and with the X-ray determination carried out by Dr. Brill at Oppau, using the Debye Scherrer method, which indicated the absence of many small primary particles, forming those microscopically visible, and thus permitting the inference that the particles were, in fact, massive, and possessing smooth sides.

⁶ It was found desirable to bring the powder to a high state of purity, but not absolutely pure. By a day's continued reduction and evacuation it was possible to render the powder extremely active both as an adsorbent and for the decomposition of ammonia. These properties imparted to the powder by the removal of the last traces of oxygen, diminished slowly when the powder was maintained in high vacuo, probably due to the unavoidable evolution of gas from the walls of the container, the diffusion of traces of gas from the interior of the metal, etc. On the other hand, powders which were not 100 per cent. clean were more readily prepared, were more reproducible and permanent, so that the use of such preparations proved a satisfactory compromise.

⁷ See I. Langmuir, *Z. angew. Chem.*, **43**, 296, 1930.

⁸ Compare Farkas (*Z. physik. Chem.*, **14B**, 371, 1931), who found that for the *Para* H₂ conversion on a tungsten surface it was necessary to clean the tungsten in an analogous way.

the further investigations on adsorption and as contact material. In Fig. 2 is shown the reproducibility of the H_2 adsorption on such "activated" powders prepared from the same original material.

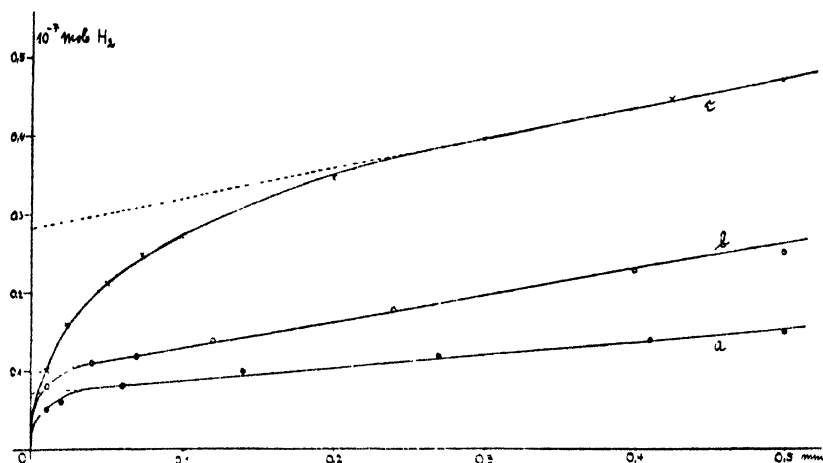


FIG. 1.—Specific adsorptive capacity of tungsten powder (C83) for H_2 at $200^\circ C$. with increasing degrees of prior treatment.

Curve a (●) After 1 hour's reduction } with H_2 of 760 mm. pressure and
 " b (○) " 3 hours " } approximately 4 hours' outgassing
 " c (×) " 8 " " } in high vacuum at 750° .

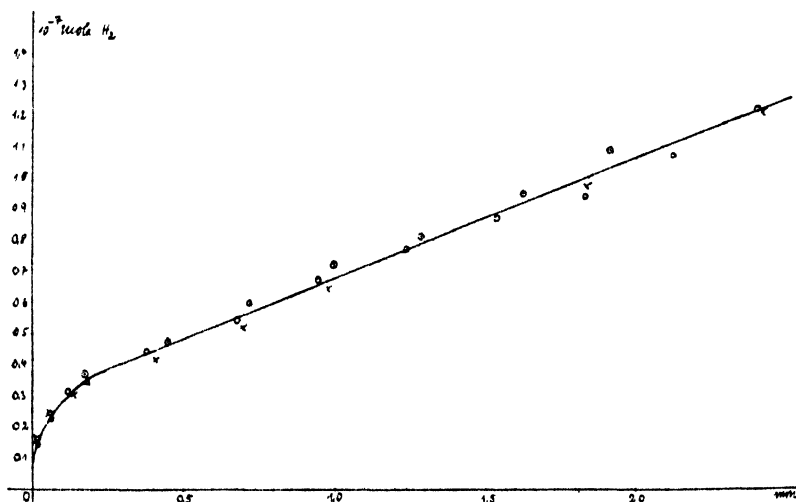


FIG. 2.—Specific adsorptive capacity of "active" tungsten powder (C83) for H_2 at $150^\circ C$.

● Experiment 42. × Experiment 43. ○ Experiment 46.
 Δ Experiment 47. ⊙ Experiment 49.

Adsorption experiments on tungsten powders of different particle size⁹ after similar pretreatment showed a similar agreement for every particular powder (*cf.* Fig. 3), and qualitatively similar results to that obtained with the preparation C83 which was generally used. The

⁹ Obtained likewise from the Osram Co.

adsorptive and catalytic powers were not quantitatively similar on account of the differences in their specific surfaces and surface structure.

In the following table (I.) are shown some characteristic values of different but similarly pretreated powders.

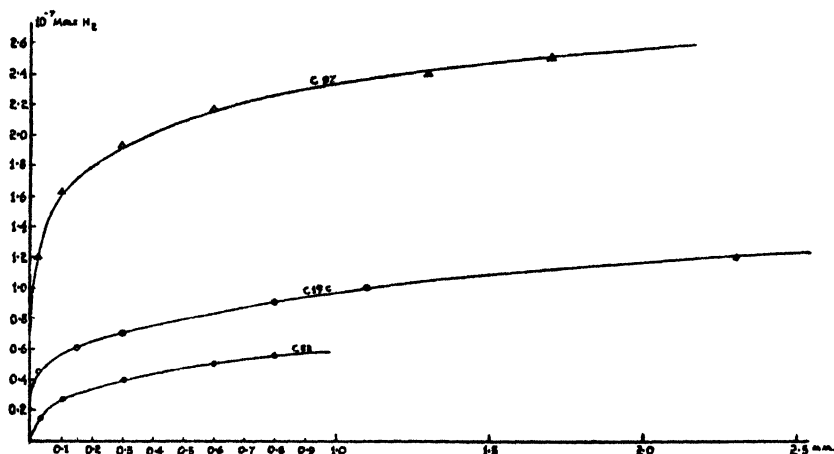


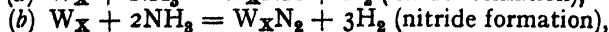
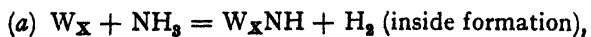
FIG. 3.—Specific adsorptive capacity of different "active" preparations of tungsten at 200° C. for H_2 .

TABLE I.

Powder.	Mean Edge Length of Particle in cm.	Specific Surface per gm. in cm. ²	Specific Adsorption for H_2 at 180° C. and 0.1 mm. in moles.	
			Per gm. Powder.	Per cm. ² of Surface. ¹⁰
C97 . .	$0.60 \cdot 10^{-4}$	5200	$1.60 \cdot 10^{-7}$	$3.1 \cdot 10^{-11}$
C19 c . .	$1.20 \cdot 10^{-4}$	2500	$0.60 \cdot 10^{-7}$	$2.4 \cdot 10^{-11}$
C83 . .	$1.86 \cdot 10^{-4}$	1700	$0.24 \cdot 10^{-7}$	$1.4 \cdot 10^{-11}$

2. Behaviour of Hydrogen and "Active" Tungsten.

Not only does the quantitative determination of the adsorptive power of tungsten powder for hydrogen serve as a suitable means for defining and reproducing the degree of activity, but the determination of the H_2 adsorption isotherms is also necessary to evaluate other measurements, chiefly those on the decomposition of ammonia. In those reactions the hydrogen set free according to



is not liberated quantitatively into the gas space, but a certain portion remains adsorbed on the metal. Thus, in order to evaluate the degree

¹⁰ It is evident that there is no rigid proportionality between the total surfaces of different samples and their adsorptive powers under similar conditions; the adsorptive power unit of surface rises apparently with decrease in particle size. This is to be expected, as the specific structure of the surface varies with the nature of the powder.

of decomposition from the increase in the hydrogen content in the gas space, obtainable from pressure readings, an exact knowledge of the quantity of adsorbed hydrogen is necessary.

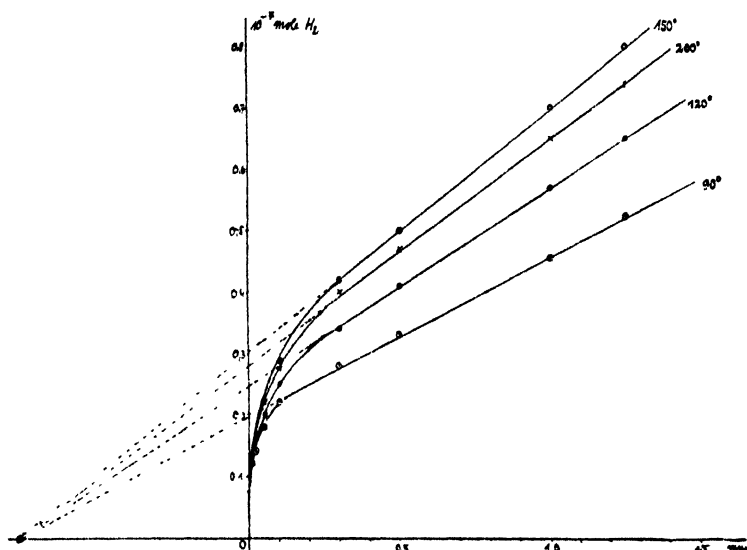


FIG. 4.—Specific adsorptive capacity of "active" tungsten powder (C83) for H_2 at different temperatures.

The isotherms in Fig. 4 and the isobars in Fig. 5 show the adsorptive power for hydrogen as affected by pressure and temperature of the pretreated "activated" powder C83.

In comparison with the normal behaviour of the adsorption of gas on solid surfaces in the region of low pressures, this adsorption of hydrogen on active tungsten surfaces reveals two remarkable features:—

(1) The quantity adsorbed does not increase proportionally to the pressure (no linearity as anticipated from Henry's law) especially in the region of lowest pressures 0.0–0.5 mm.

(2) Within a certain range of temperature at a definite pressure the amount of hydrogen adsorbed in

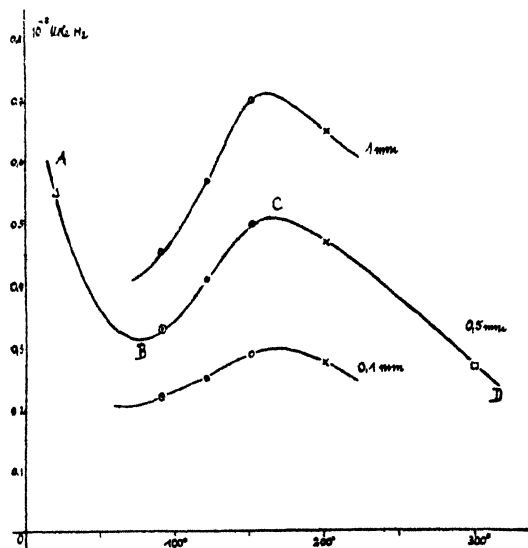


FIG. 5.—Specific adsorptive capacity of "active" tungsten powder (C83) for H_2 in relation to temperature (Isobars).

equilibrium increases with increase in temperature in contradistinction to the inverse dependence on temperature of normal adsorption. Hydrogen adsorption on active tungsten surfaces is apparently another example of that adsorption which recently H. S. Taylor¹¹ has noted and designated "activated adsorption" in a whole series of systems, especially those in which catalytic reactions participate. The interaction between metal surface and hydrogen is apparently different at high temperatures to that at low. In a transitional range (on activated powder C83 between 90° and 150°) the "normal" adsorption is replaced in increasing extent, *i.e.* on an increasing area of surface by the "activated" adsorption or formation of a surface hydride.

In the region AB the "normal" adsorption is exerted on the hydrogen molecules by Van der Waals' forces at the tungsten surface. In the

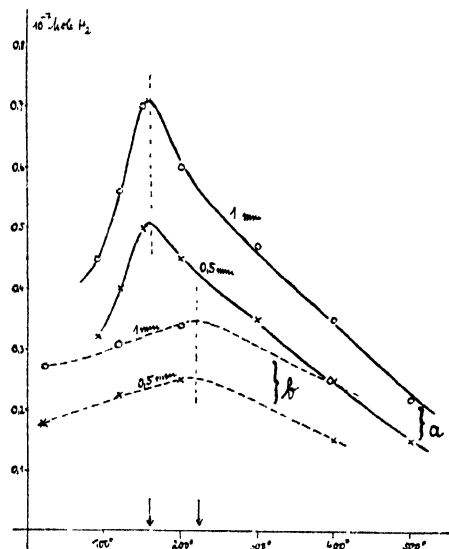


FIG. 6.— Specific adsorptive capacity of tungsten powder (C83) for H_2 in a condition of (a) greater and (b) lesser activity in relation to temperature. (Isobars).

active patches with increase in temperature is noted in a similar way in the combination with nitrogen as well as in the decomposition of ammonia on tungsten surfaces (see pp. 235 and 239). To all appearances this is an important and hitherto neglected factor in several surface reactions.

That this phenomenon is connected with the number of active centres on the metallic surface is demonstrated by the fact that it is markedly dependent on the state of reduction and evacuation of the surface.

(1) With decreasing attention to the cleanliness of the powder, the steep increase in the adsorption isotherm before the region where Henry's law holds is less prominent (*cf.* Fig. 1).

(2) The abnormal temperature dependence of the maximum of the gas adsorption in the isobars is flattened out with less clean powders, and shifted to the region of higher temperatures (*cf.* Fig. 6).

The interpretation of these results will not be gone into here, since the accurate determination of the hydrogen adsorption, especially its

region CD a markedly stronger linkage between the hydrogen and the metal (tungsten hydride) especially in the active portions of the metal surface is more dominant, and only comes into existence with the supply of an energy of activation. In the intermediary region, BC, there is apparently no true equilibrium which is confirmed by the fact that when the state C has been established, a lowering of the temperature does not reduce, but increases, the amount of hydrogen taken up. The portion of the curve BC is thus not reversible.

It is remarkable, and at present inexplicable, that in the region BC as the temperature rises, increasing portions of the metallic surface are rendered accessible to activated adsorption or hydride formation. Such an increase of the

¹¹ *J.A.C.S.*, **53**, 3604, 1931; *Chem. Rev.*, **2**, 1-44, 1931.

reproducibility, suffices for these investigations, especially for the study of the kinetics of the decomposition of ammonia on tungsten.

3. Behaviour of Molecular Nitrogen and "Activated" Tungsten.

Investigations on the system of gaseous nitrogen by reduced and evacuated nitrogen have been carried out by one of us (F.), and G. Messner and the main results already published.¹² The system W — N₂ shows even more clearly than the system W — H₂ the dual character of the surface linkages in that at low temperatures there is a relatively weak adsorption of the nitrogen molecule. On raising the temperature, a more stable compound is formed, in our view a local surface tungsten nitride. In this case also there is an intermediary region ($\sim 20^\circ$ to $\sim 600^\circ$ C.) in which on elevation of the temperature there is an increase in the nitrogen uptake which is not reversible on lowering of the temperature. On further increase of the temperature, a normal reversible decrease in the amount of nitrogen combined with the metal sets in ($\sim 600^\circ$ to 1000° nitride decomposition).¹³ As in the case of the union of hydrogen to form a hydride, the rapid increase of the surface available for nitride formation with increase in the temperature is theoretically unexplained.

4. Adsorption of Ammonia on "Activated" Tungsten.

In Fig. 7 are depicted the adsorption isotherms of ammonia on the activated powder C83 over the temperature range 20° to 60° C., and a pressure range of $5 \cdot 10^{-3}$ to 0.2 mm.¹⁴ In this case also at low pressures there is a steep rise in the quantity of adsorbed gas, which terminates on increasing the pressure in a linear and less steep adsorption which is proportional to the pressure (region of Henry's law). This linear increase continues unchanged up to considerably more elevated pressures (Fig. 8), but eventually in the region 200 to 300 mm. renews a somewhat steeper inclination. This phenomena,

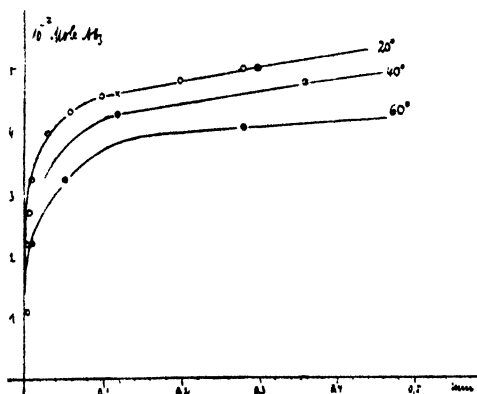


FIG. 7.—Specific adsorptive capacity of "active" tungsten powder (C83) for NH₃ at different temperatures.

¹³ Z. physik. Chem., Bodenstein Festband, 593, 1931.

¹⁴ For detailed quantitative results, see Messner and Frankenger, *loc. cit.* The dual character of the union of the nitrogen to the metal (normal—a relatively weak union, strong—a chemical union) is indicated by the following experiment with a tungsten powder saturated with nitrogen at a definite temperature. On rapid elevation of the temperature there is at first a rapid increase in pressure, which is followed by a definitely slower decrease in pressure, this latter finally exceeds the instant increase in pressure. Apparently these opposing pressure changes represent a rapid desorption, followed by a slower chemical union of the nitrogen.

¹⁴ Measurements of the ammonia adsorption at pressures $< 5 \cdot 10^{-3}$ mm. were difficult to execute, in spite of the sensitivity of the method; (a Pirani hot wire manometer), since apparently on account of a slight decomposition of the adsorbed gas even at these temperatures (60°) an increase in the hydrogen pressure to 10^{-3} mm. was observed.

analogous to many measurements of a similar character, is to be regarded as condensation of the ammonia in the adsorptive layer. There is thus no question of a sharply defined adsorption saturation of the metallic surface; the quantities of ammonia taken up at high pressures by the metallic powder are likewise temperature dependent. Nevertheless, a rough comparison of the computed surface of the powder with the area occupied by the ammonia adsorbed at equilibrium at the high pressures possess a certain interest.

One gm. of the "activated" powder C83 adsorbed at 20° C., and pressures from 300 to 500 mm. Some 11 to 21 10^{-7} moles. NH_3 which, with a molecular area for the NH_3 molecule of $\sim 10 \cdot 10^{-16}$ mm^2 ,¹⁵ represents an area of from 660 to 1260 mm^2 , whilst the macroscopically determined area of the powder was some 1700 cm^2 . Since this latter value

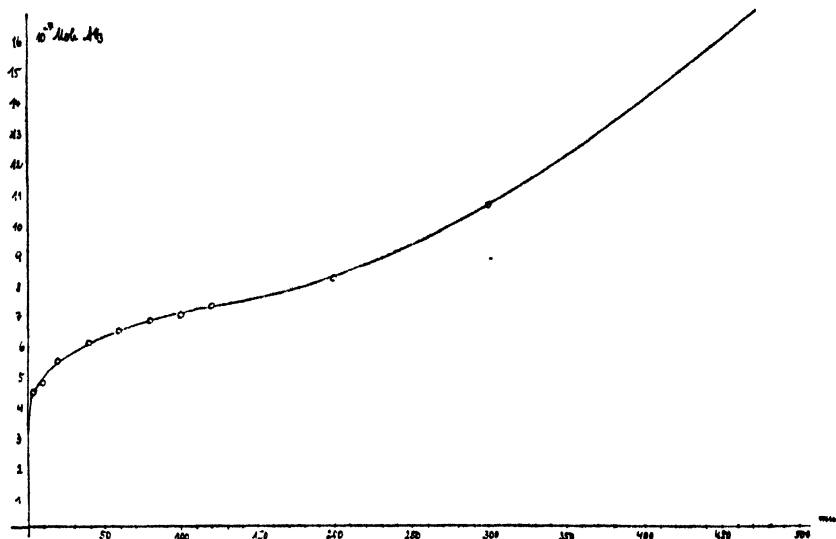


FIG. 8.—Specific adsorptive capacity of tungsten powder (C83) for NH_3 at 20° C.

is a lower limit, we conclude that it is probable that the adsorption of ammonia on the metal surface attains eventually a molecular layer.¹⁶

The kinetics of the ammonia decomposition were examined on activated tungsten at very low pressures with the object of simplifying the dissection of the kinetics of the elementary processes taking place by eliminating all transport and adsorptive processes through employing as initial system an adsorbed ammonia film. It was therefore important to discover to what extent at these low pressures in the temperature range of decomposition employed (90° to 200° C.) there was, in fact, a practically completed adsorption of the gas on the activated powder C83. Naturally, the extrapolation of the values for the adsorption to the range 90° to 200° from measurements at 20° to 60° is attended with some uncertainty, since the temperature coefficient of the adsorption

¹⁵ Cf. M. Gona, *Physik. Z.*, **20**, 14, 1919; H. G. Grimm, *Z. Elektrochem.*, **31**, 47a, 1925; Mark-Pohland, *Z. Kristallog.*, **61**, 532, 1925.

¹⁶ Adsorption experiments on the tungsten powder C19 c (specific surface, 2500 cm^2) reveal a remarkable agreement between the surface and the area occupied by the adsorbed ammonia at saturation ($3 \cdot 0 \times 10^{-6}$ moles. per gm. powder at 20-300 mm. pressure) corresponding to a specific surface of 1800 cm^2 .

equilibrium and thus the heat of adsorption varies with the extent of adsorption. Nevertheless, it is possible to compute the order of the adsorptive equilibrium from the initial stages of the decomposition experiments, *i.e.* by admitting relatively small quantities of ammonia (sometimes 10^{-6} mole.) to a quantity of tungsten (10 gms.) at different temperatures, *e.g.* for a surface concentration of $1 \cdot 10^{-7}$ moles. $\text{NH}_3/\text{gm.}$ from the equilibrium pressures between 20° and 60° , a heat of adsorption from 8000 to 14,000 cal. was obtained. The ammonia pressures corresponding to these surface concentrations at different temperatures, can be calculated in the well-known manner. They are:—

For 8000 Cals.		For 14,000 Cals.	
90°	0.03 mm.		0.30 mm.
120°	0.08 "		1.13 "
150°	0.16 "		3.55 "
200°	0.42 "		15.9 "

Thus conditions of complete adsorption is only approximated to at the lowest temperatures of decomposition, at the higher temperatures this is not the case.

5. Behaviour of these Gases on Simultaneous Adsorption or Combustion with Tungsten.

After the behaviour of H_2 , N_2 and NH_3 on "activated" tungsten had been established sufficiently well for the purpose of this investigations, it was necessary on account of the conditions obtaining in the decomposition of ammonia to examine what might be the mutual effects of the gases on simultaneous adsorption or combination with the tungsten, and how far the surface products (tungsten nitride and imide) formed in the decomposition of ammonia modified the results obtained in the clean activated powder.

(a) *Experiments in the mixed adsorption of hydrogen and ammonia on tungsten* showed that both gases were adsorbed uninfluenced by each other. Thus, the hydrogen pressure of a hydrogen charged powder did not allow on the addition of from 1 to 610^{-6} moles NH_3 . This independence of the hydrogen and ammonia adsorption is noted also in the experiments on the decomposition of ammonia, since both the quantity and rate of decomposition were entirely uninfluenced by the presence of hydrogen (0.2 mm.).

(b) *Investigations on the behaviour of hydrogen on tungsten* which had been covered with relatively large quantities of the surface products resulting from ammonia decomposition revealed an increase in hydrogen adsorption compared with the clean "activated" powder. This effect, doubtless very important in the catalytic *synthesis* of ammonia,¹² is only marked on those powders which are covered with relatively large quantities of the surface products, the nitride and the imide. With small concentrations¹⁷ of the decomposition products resulting at the stage to which the rate of ammonia decomposition was followed kinetically no difference in the adsorptive power of the nitride and imide containing metal and the pure metal could be detected (see Fig. 9).

Within this range of concentration the decomposition of ammonia can be evaluated with the end of the observed hydrogen adsorptions on the clean "activated" powder. Decomposition experiments outside these ranges of ammonia adsorption were not carried out.

¹⁷ The highest concentration of surface products at which still no alteration in the hydrogen concentration was noted was from 10×10^{-7} moles. $\text{NH}_3/\text{gm.}$ powder at 200°C.

(c) Certain indications were found that the adsorption of ammonia was likewise influenced by the coating of the tungsten with surface products. Especially prominent was the fact that with increasing formation of tungsten imide and tungsten nitride (progressive decomposition of the ammonia), an ever-increasing quantity of ammonia was adsorbed in the tungsten surface. Since this excess ammonia adsorbed on progressive chemical alteration of the metallic surface in contrast to the ammonia on the clean metal is *not decomposed*, we may suggest that this adhering ammonia is found in a special manner (possibly as a result of complex formation with the nitride which has been formed). Experiments on the

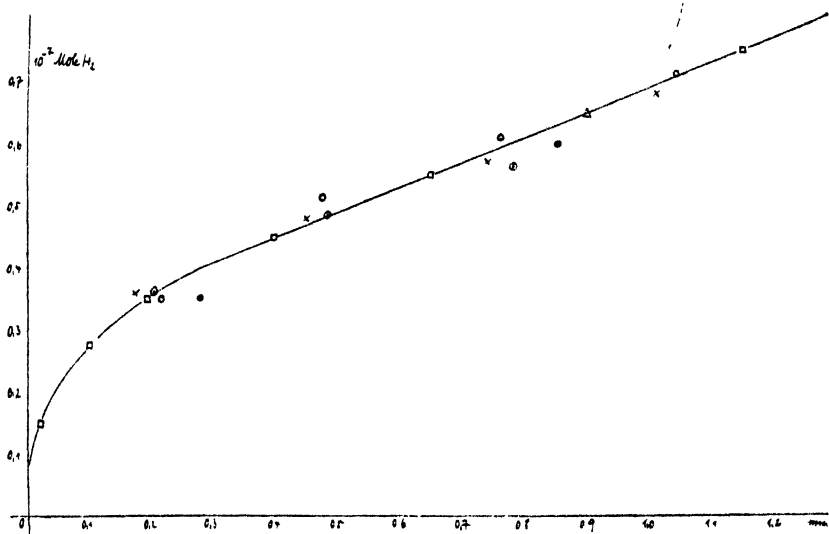


FIG. 9.—Specific adsorptive capacity of "active" tungsten powder covered with NH_3 and its decomposition products (C83) for H_2 at 150° .

Sign.	Exp.	Total NH_3 Content per gram of Powder.
Δ	50	4.78×10^{-7} mole.
\bullet	51	5.57×10^{-7} "
\times	51	7.16×10^{-7} "
\odot	51	8.75×10^{-7} "
\circ	51	9.55×10^{-7} "
\square	Isotherm figures of the pure "active" powder at 150°C .	

direct measurement of the ammonia adsorption on strongly nitride containing surfaces are in progress.

6. Decomposition of Ammonia on Tungsten Surfaces with Formation of Tungsten Nitride and Tungsten Imide (First Stage in the Decomposition Catalysis) and the Kinetics of this Decomposition in the Adsorbed Layer.

The following results were obtained in the experiments on ammonia decomposition. As has already been noted, these new experiments *

* Compare footnotes 1 and 12; see further A. Mittasch and W. Frankenburger, *Z. Elektrochem.*, **35**, 920, 1929; A. König and O. Wagner, *Z. physik. Chem.*, **A144**, 213, 1929; C. H. Kunsman *et al.*, *Phil. Mag.*, **10**, 1015, 1930; P. H. Emmett and Burnauer, *J.A.C.S.*, **52**, 2682, 1930; P. H. Emmett, *J. Chem. Educ.*, **7**, 2571, 1930; and G. M. Schwab and H. Schmidt, *Z. physik. Chem.*, **B3**, 337, 1929.

indicate that the catalytic synthesis and decomposition of ammonia proceed through the intermediary stages of imide and nitride formation. The yield and velocity of this imide and nitride formation were determined by observation of the decomposition of relatively small quantities of ammonia admitted to a definite quantity of active tungsten powder over the temperature range 90° to 250° C. in which the formation of these surface compounds¹⁸ with liberation of hydrogen occurs, and in which there is practically no further decomposition. The surface reactions occurring are limited to specific portions of the metallic surface. After nitride formation these portions are blocked, and serve as centres of decomposition. This renders it possible to completely exhaust the metallic surface by progressive reaction with equal and small doses of ammonia (8×10^{-7} mole to 10 gms. tungsten powder of 17,000 cm.² specific surface), and measure each individual decomposition and reactivity. Since on decomposition of each of these doses of ammonia hydrogen is given off in the gas phase with the necessary correction for the amount of hydrogen adsorbed, the reaction velocity of decomposition of each successive dose of ammonia can be evaluated. In general, the decomposition of such a dose reveals a composite process. A part of the ammonia decomposes in a bimolecular manner (a), a second portion in a monomolecular fashion (b), with the formation of imide and nitride and hydrogen liberation, whilst the residue (c) remains undecomposed. By following the decomposition of individual doses at a definite temperature until the metallic surface is covered, *i.e.*, to the stage in which further adsorbed doses remain entirely

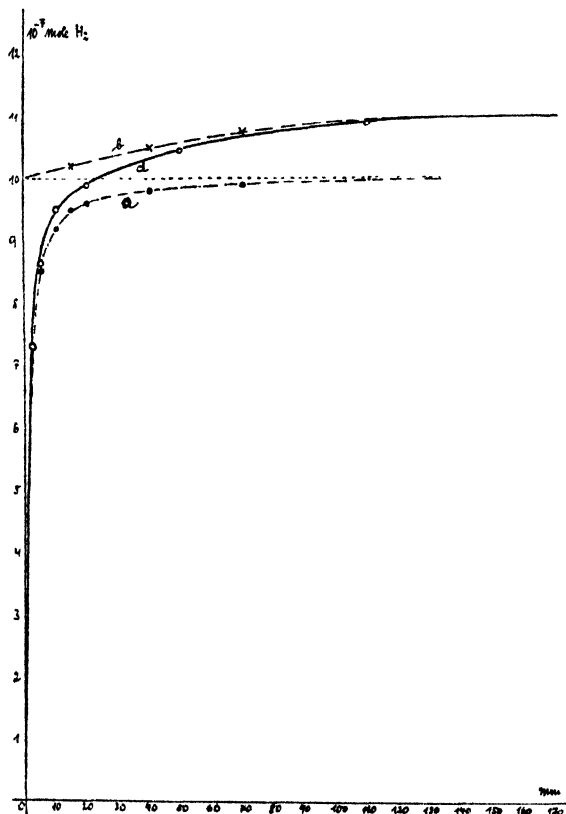


FIG. 10.—Ammonia decomposition on "active" tungsten powder (C83) at 150° .

- a bimolecular fraction $k_a = 11.0 \times 10^{-4}$ (reckoned as H_2).
 b monomolecular fraction $k_b = 6.7 \times 10^{-3}$.
 c experimental figures.

evaluated. In general, the decomposition of such a dose reveals a composite process. A part of the ammonia decomposes in a bimolecular manner (a), a second portion in a monomolecular fashion (b), with the formation of imide and nitride and hydrogen liberation, whilst the residue (c) remains undecomposed. By following the decomposition of individual doses at a definite temperature until the metallic surface is covered, *i.e.*, to the stage in which further adsorbed doses remain entirely

¹⁸ We denote further by "nitride" all the surface products formed in the decomposition of ammonia, *viz.*, tungsten nitride and tungsten imide.

undecomposed, we can estimate the total amount of bimolecularly and unimolecularly decomposed, and the undecomposed ammonia, *i.e.*, Σa , Σb and Σc .

The following may be stated concerning the kinetics and the quantity relationships of the quantities *a*, *b* and *c* of a single decomposition. At

TABLE II.—EXP. 47. NH_3 DECOMPOSITION AT 150° .

Ad- mission.	NH_3 in 10^{-7} mol.	Decomposed as Unimolecular. Per Cent.	k_a .	Decomposed as Bimolecular. Per Cent (referred to H_2).	k_b .	Unde- compos NH_3 . Per Cent.
1	7.96	—	—	100	$112 \cdot 10^{-4}$	—
2	7.96	6.7	$6.7 \cdot 10^{-3}$	88.8	110	4.5
3	8.00	8.3	6.7	83.2	110	8.5
4	7.96	11.7	6.7	68.0	112	20.3
5	7.96	13.4	6.7	54.5	110	32.1

a definite temperature the velocity constants k_a and k_b of the bimolecular nitride and the unimolecular imide formation are characteristic values independent of the specific structure of the tungsten surface.

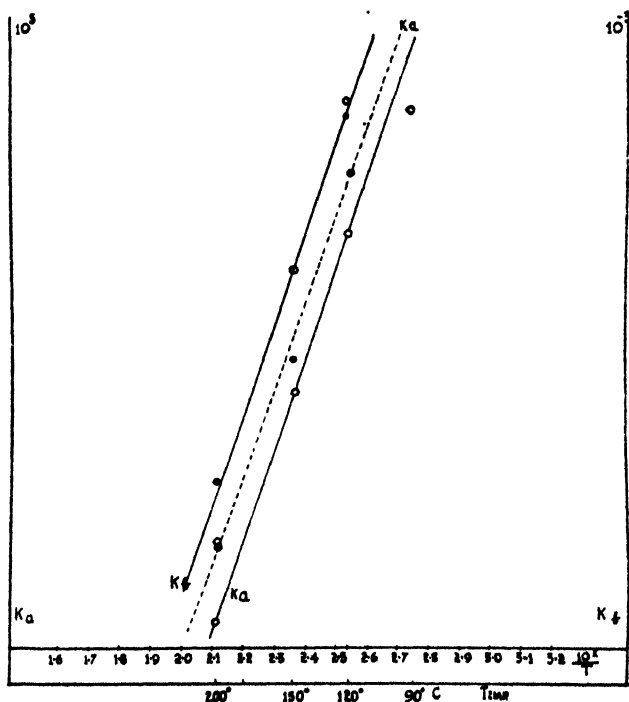


FIG. 11.—Temperature coefficient of ammonia decomposition on "active" tungsten powder (C83).

k_a and k_b . Figures from experiments with 10 g. powder (○) and 17 g. powder (●). The bimolecular constants k_b relate to NH_3 .

They are not affected by the degree of activity conferred in the preparation or by the extent of blocking of the tungsten surface by prior nitride formation or poisoning (*e.g.*, with O_2 , H_2O). In addition, the temperature coefficients of k_a and k_b are independent of the state of the metallic surface. These were found somewhat unexpectedly to be identical for k_a and k_b with an activation energy of 12,000 cal.

In contradistinction to this lack of sensitivity of the velocity constants to the nature of the surface the *absolute* values of a , b and c , *i.e.*, the distribution of a definite amount of ammonia into bimolecular and monomolecular decomposition products and undecomposed residue at definite temperature varies greatly with the state of the metallic surface. On fresh (*i.e.*, well-reduced and evacuated) metal which has not had any prior treatment with ammonia, the bimolecular reaction a predominates. With increasing blockings of the tungsten with nitride formed in the decomposition or with metal already poisoned (*e.g.*, with oxygen) a becomes less at the expense of b and c until finally on rich nitride or strongly poisoned metals only a small portion of the reacting ammonia decomposes in a unimolecular manner, and finally it all remains undecomposed.

With the metal surfaces in similar original states and at definite temperatures for a series of admissions 1, 2, 3 . . . n , the fractions of ammonia decomposed and undecomposed ($a_1 a_2 a_3 \dots a_n$, $b_1 b_2 b_3 \dots b_n$, $c_1 c_2 c_3 \dots c_n$) are found to be reproducible so that the sum of these fractions (Σa , Σb , Σc) is found to characterise the surface and $\Sigma a + \Sigma b$ is a measure of the nitride forming power of the surface. If we examine the decomposition at metal surfaces in identical original states at different temperatures, we find that at these similar metallic surfaces the net nitride formation ($\Sigma a + \Sigma b$) increases with the temperature. The

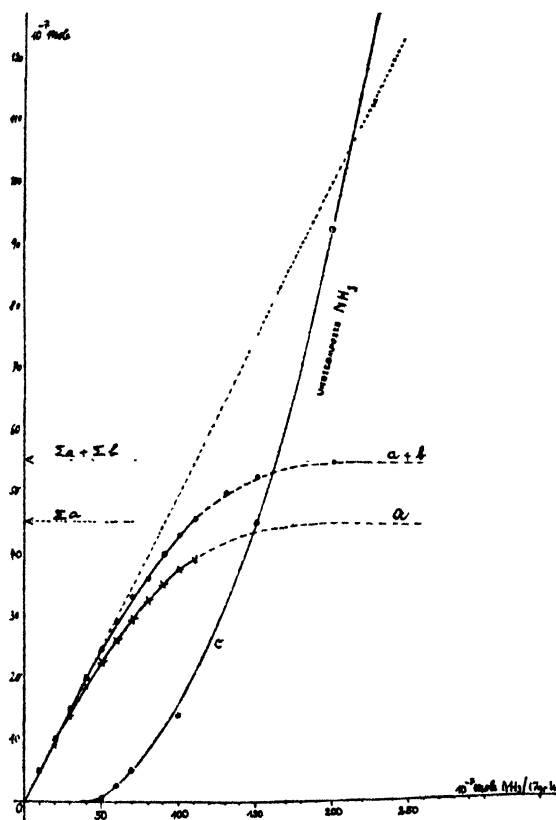


FIG. 12.— NH_3 balance of the NH_3 decomposition experiments on "active" tungsten powder (C83) at 200° .

- $\Sigma (a + b)$ Total nitride formed of the 1st and 2nd order.
- $\Sigma (a)$ of the 2nd order.
- $\Sigma (c)$ the undecomposed ammonia residue.

faculty for nitride formation of a given surface is therefore dependent on the temperature. This is contrary to the assumption that the areas

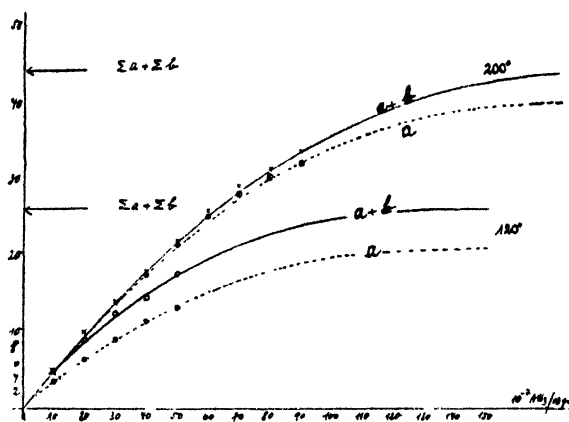


FIG. 13.—Nitride formation in relation to NH_3 concentration on "active" tungsten powder (C83) at different temperatures.

predisposed to two formations of intermediary products (i.e., active patches of a catalytic surface) are determined by their structure and independent of the temperature. Here also we encounter the same phenomenon that we established in the formation of tungsten hydride, and tungsten nitride from $\text{W} + \text{H}_2$ and $\text{W} + \text{N}_2$. The fraction of a given surface capable of entering into chemical

reaction (formation of surface compounds) reacts not only more rapidly, but also grows with increase of temperature. We shall attempt to give a theoretical treatment of these measurements, especially on the kinetics of the decomposition of ammonia, in another place; this work includes only the important experimental results.

ON ADSORPTION AND REFLECTION PROCESSES IN THE INTERACTION OF HYDROGEN AND METALS.

By K. F. BONHOEFFER AND A. FARKAS.

(From the Institute of Physical Chemistry of the University of Frankfurt a/M.)

Received 19th November, 1931.

The basis of the following communication is the conception that in the adsorption of hydrogen on some metallic surfaces the bond between the atoms in the hydrogen molecule becomes loosened to such an extent that the individual atoms are bound more firmly to the metal than to each other. We shall speak of this kind of adsorption as "atomic" adsorption. This conception has received general recognition in the case of platinum, for instance, and we shall extend it to cover the other metals treated here. Atomic adsorption is not due to van der Waals' attractive forces between the hydrogen molecules and the atoms of the metallic surface, but depends on forces similar to those assumed by Slater¹ to explain metallic cohesion.

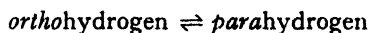
¹ J. C. Slater, *Physic. Rev.*, **35**, 509, 1930.

On the basis of this conception we can draw certain conclusions with regard to the processes of reflection and adsorption at the boundary surface metal-hydrogen from the results of some new experiments dealing with catalytic *ortho-para*-hydrogen conversion by metals.^{2,3}

When a hydrogen molecule impinges on a metallic surface we may distinguish between two different processes, *viz.*, that the molecule is either reflected or adsorbed.

In the case of reflection the direction and, in general, also the velocity of the impinging molecule is changed, since the kinetic energy of the molecule is transformed into oscillatory energy of the surface atoms which have suffered impact. Baule⁴ showed that this transformation of kinetic energy into oscillatory energy takes place more readily the lighter the surface atom and the heavier the impinging atom. This follows directly from the principle of the conservation of impulse in the mechanical picture one makes of the reflection process. Consequently, we may expect a particularly weak energy exchange in the impact of hydrogen molecules on metallic surfaces. In such reflections the hydrogen molecule will not be able to change from one modification to the other, because this process does not differ from a collision with foreign atoms or molecules in the gas phase, and these collisions do not cause *ortho-para* hydrogen conversion, as we know.⁵

When adsorption occurs, the hydrogen remains some time in a loosened state on the surface, and comes into temperature equilibrium with the metal. After this period, the hydrogen evaporates, *i.e.*, it is desorbed. In the stationary condition the velocity of desorption is equal to the velocity of adsorption. The *ortho-para* hydrogen content of the hydrogen leaving the surface corresponds always to equilibrium at the temperature of the surface. It has no relation to the *ortho-para* hydrogen concentration ratio of the originally adsorbed hydrogen, because the bond in each adsorbed hydrogen molecule is loosened to such an extent that it is impossible to distinguish *ortho* from *para* hydrogen in the adsorption phase. Therefore the measured velocity of transformation



is equal to the velocity of adsorption or desorption.

Comparing the number of molecules transformed, *i.e.*, adsorbed, per second with the number impinging in the same time, we find that the former is very small compared with the latter at not too high temperatures (on platinum² up to 150° C.). It is true, the velocity of transformation measured is not exactly the real velocity, since the latter is diminished by diffusion processes. Nevertheless, this correction may be neglected, because in the temperature interval studied the velocity of diffusion far exceeds the velocity of reaction. The velocity of transformation rises rapidly with the temperature, showing that at high temperatures the adsorption processes are accelerated and the ratio of adsorbed molecules to impinging molecules increases. With platinum at about 500° C., the number of molecules adsorbed and desorbed is of the same order of magnitude as the number reflected. One might be tempted to explain the growth of the adsorption processes by assuming that the surface becomes more and more bare at higher temperatures on

² K. F. Bonhoeffer and A. Farkas, *Z. physik. Chem.*, B, **12**, 231, 1931.

³ A. Farkas, *Z. physik. Chem.*, B, **14**, 371, 1931.

⁴ B. Baule, *Ann. Physik*, **44**, 145, 1914.

⁵ K. F. Bonhoeffer and P. Harteck, *Z. physik. Chem.*, B, **4**, 113, 1929.

account of the greater velocity of desorption, and that the exclusive occurrence of reflection processes at lower temperatures is due to the fact that the impinging hydrogen always meets an adsorbed layer. But this explanation is not sufficient, because it can be shown that even when reflection processes alone occur, the metallic surface is not even approximately completely covered. In this case the apparent order of reaction of the hydrogen transformation would be zero.⁶ Since this is not in agreement with experience (on platinum the order of reaction is nearer to one than to zero³), we must conclude that at low temperatures reflection processes also occur on bare surfaces. This agrees with ideas recently developed by H. S. Taylor.⁷

Owing to the growth of the adsorption processes at the expense of reflection on increasing the temperature, the adsorption processes must contribute more to the heat exchange at the boundary surface solid gas. As a quantitative measure of the completeness of the heat exchange, Knudsen⁸ introduced the term "accommodation-coefficient" ($=a$), defined by the equation

$$a = \frac{T_2 - T_0}{T_1 - T_0},$$

where T_0 , T_1 and T_2 represent the mean temperatures of the impinging molecules, the surface and the molecules leaving the surface respectively. Since the heat exchange in reflection processes is incomplete, whereas each adsorption and desorption process results in complete exchange, raising the temperature must cause an increase in the accommodation-coefficient.

The conclusions with regard to the heat exchange based on the results of experiments dealing with the catalytic *parahydrogen* transformation are confirmed by experience. If we compare the behaviour of clean metallic surfaces with the behaviour of metallic surfaces which are already covered with a layer of adsorbed gas, we observe a characteristic effect on the accommodation-coefficient.

In so far as the heat exchange results from reflection processes (that is at low temperatures) adsorbed layers of foreign gases or surface compounds always cause an increase in the accommodation-coefficient^{2, 3, 9} in agreement with the theory of Baule.⁴ If, however, adsorption and re-evaporation processes come into play in the heat exchange on clean metals, adsorbed layers retard the heat exchange and result in a lowering of the accommodation-coefficient. As a result, we may expect to find that the accommodation-temperature curves on clean and covered metallic surface intersect. As Fig. 1 shows this is actually observed (see Fig. 1, in which, however, the heat given up from a tungsten wire per second, and not the accommodation-coefficient itself, is plotted as a function of temperature).

In analogy with the behaviour of adsorbed foreign gas layers, adsorbed hydrogen itself must exert an influence on the accommodation-coefficient. An investigation carried out from this standpoint led to a surprising result in the case of nickel. With increasing hydrogen pressure the

⁶ C. N. Hinshelwood, *The Kinetics of Chemical Change in Gaseous Systems*, Oxford, 1929, p. 211.

⁷ H. S. Taylor, *J. Amer. Chem. Soc.*, **53**, 578, 1931.

⁸ M. Knudsen, *Ann. Physik*, **34**, 593, 1911.

⁹ D. R. Hughes and R. C. Bevan, *Proc. Roy. Soc. A*, **117**, 101, 1928; D. L. Chapman and W. K. Hall, *ibid.*, **A. 124**, 478, 1929; J. K. Roberts, *ibid.*, **A. 129**, 146, 1930; *This vol.*, 395.

accommodation-coefficient increases discontinuously at a certain density of adsorption. The pressure at which this sudden change in the coefficient occurs depends on the temperature. We find the same discontinuous behaviour in the catalysis of the *parahydrogen* transformation. The catalytic activity falls discontinuously at the same point as the break in the accommodation-coefficient curve.

This phenomenon may be explained as follows: When the density of the adsorbed layer of hydrogen has reached a certain value (which

may be considerably removed from saturation), an attempt to raise the density of adsorption further, causes continuous regions of denser occupation of constant composition to form on the surface. The conditions are similar to those which have been observed in two-dimensional condensation.¹⁰ In our case, however, it appears to be more to the point to speak of the formation of chemical hydrides which exert a definite decomposition pressure (see Fig. 2). This receives particular support from experiments of Davisson and Germer,¹¹ and of Rupp,¹² who were able to demonstrate a nickel-hydrogen lattice by means of electron diffraction. From the latter experiments it appears to be indicated that these hydrides are not present merely in the form of two-dimensional compounds, but that the hydrogen has penetrated the lattice of the metal to a depth of several atomic layers. It should be noted, however, that our hydride cannot be identical with the hydride detected by electron diffraction, since the latter is capable of existence at much lower pressures.

In this hydride formation the hydrogen is more rigidly bound, resulting in a smaller velocity of evaporation and a lower catalytic activity. In agreement with this, we find that the catalysis on the hydride surface

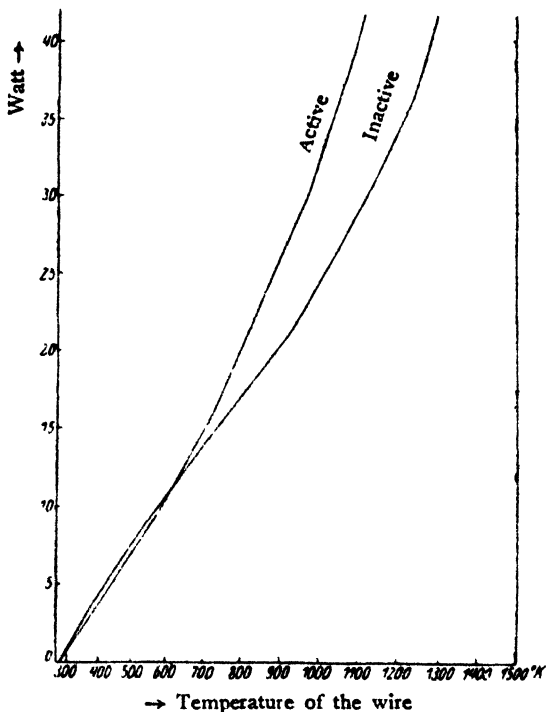


FIG. 1.—Heat exchange on a tungsten wire. Under 650° K the heat given up by an inactive (oxygen covered) wire is about 20 per cent. more than that given up by an active (clean) wire (heat exchange by reflection only), at higher temperatures we find the reverse to be true (heat exchange by adsorption). The heat exchange curve of clean and inactive (toluene poisoned) platinum is similar to above.

¹⁰ J. Langmuir, *J. Amer. Chem. Soc.*, **39**, 1883, 1917; N. K. Adam, *Proc. Roy. Soc., A*, **99**, 336, 1921; A. Marcellin, *Ann. Physique*, (10) **4**, 459, 1925.

¹¹ L. H. Germer, *Z. Physik*, **54**, 408, 1929.

¹² E. Rupp, *Z. Elektrochem.*, **35**, 537, 1929.

shows a greater temperature coefficient than that on a clean surface, in

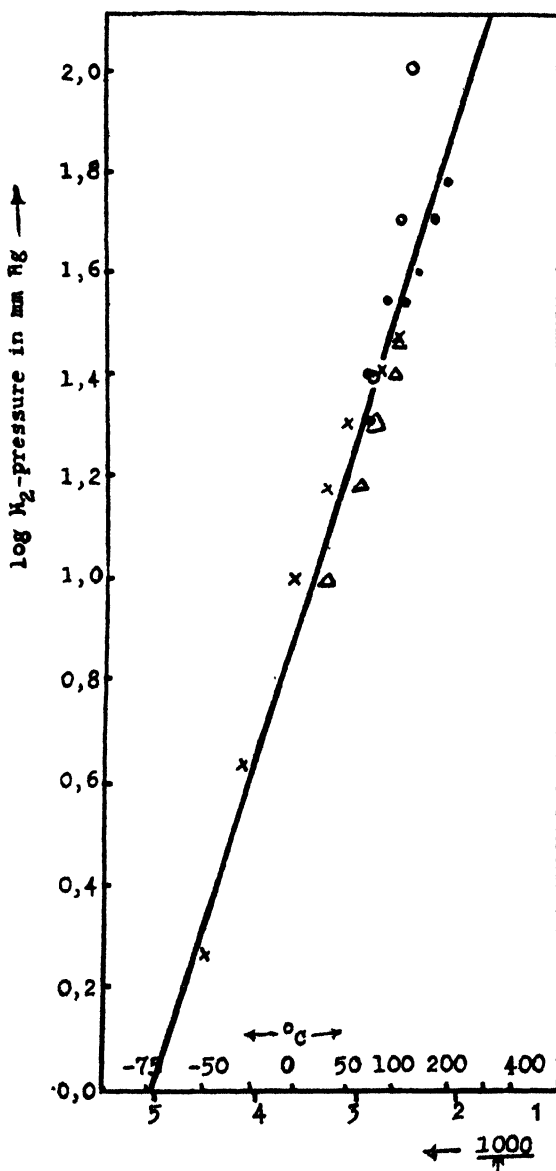


FIG. 2.—Decomposition pressure of nickelhydride

The points and circles refer to the discontinuities observed in the catalysis on two different wires; the crosses and triangles refer to those in the heat exchange.

¹³ A. Farkas, *unpublished experiments*.

¹⁴ H. H. Rowley, *unpublished experiments*.

¹⁵ K. Rummel, *unpublished experiments*.

¹⁶ The charcoals used were so-called "oxygen-covered charcoals" (cf. A. Frumkin, *Kolloidzeitschr.*, 51, 123, 1930), and it is possible that "hydrogen-charcoals" behave differently.

consequence of the consolidation of the hydrogen bond.

Similar discontinuities were found in investigations on the heat exchange on iron¹³ and platinum,¹⁴ so that in these cases, too, hydride formation is indicated.

In conclusion, we would refer to the result of some experiments on the adsorption of hydrogen and the catalysis of *para*-hydrogen on charcoal.¹⁵ In this case, it has been found that the adsorption of hydrogen is molecular, in contrast with our assumption of atomic adsorption on metals; for it is possible to adsorb and desorb hydrogen on charcoal without the ratio of *ortho-para* hydrogen adjusting itself to the equilibrium corresponding to the temperature of the charcoal. This behaviour would be impossible in the case of atomic adsorption. Adjustment of the equilibrium between the *ortho* and *para* hydrogen concentration takes place in the adsorption layer with a velocity which may vary according to the nature of the charcoal.¹⁶ Very different velocities of transformation are observed

with charcoals which otherwise exhibit the same adsorptive capacity with regard to hydrogen.

Measurements of the velocity of transformation in the adsorbed phase between -167 and -210° show that the reaction velocity does not depend appreciably on the temperature. When we take into consideration that the quantity of hydrogen adsorbed decreases strongly on raising the temperature, we see that a given quantity of charcoal catalytically transforms less hydrogen at higher than at lower temperatures. This explains the apparent negative temperature coefficient of the *para*-hydrogen catalysis found with charcoal, which is due to the different state of hydrogen adsorbed on charcoal compared with metals.

ACTIVATED ADSORPTION OF HYDROGEN AND THE PARA-HYDROGEN CONVERSION.

BY HUGH S. TAYLOR AND ALBERT SHERMAN.

Received 19th December, 1931.

A variety of recent researches¹ on adsorption has indicated that a given gas may be absorbed on a given surface in two different modes of binding each with its own characteristic extent and energy of binding. The low temperature adsorption is rapid, and, in the cases examined, involves relatively low heats of adsorption; this adsorption we term van der Waals' adsorption. The higher temperature adsorption proceeds, at suitable temperatures, at measurable speeds increasing exponentially with temperature, from which velocities an activation energy of adsorption may be calculated. Equilibrium data are only obtainable at sufficiently high temperatures. The heat of adsorption is, in these cases, normally one order higher in magnitude than the low temperature adsorption. We have termed this type of adsorption "activated adsorption."

The parallelism existing between the capacity of surfaces to show activated adsorption and their capacity to produce chemical reactions between such adsorbed gases and other reactants led us to the conclusion that activated adsorption is an essential preliminary to surface reaction. The *ortho*-, *para*-hydrogen interconversion seemed to offer to us a simple process whereby our knowledge of the modes of adsorption of hydrogen to different surfaces might be utilised to correlate adsorption and chemical change at surfaces. There is definite evidence in the original work of Bonhoeffer and Harteck² on the spin-isomerisation of hydrogen that a specific effect of surfaces exists in this interconversion analogous to that obtaining in chemical reactions. Accordingly, we have tested a variety of surfaces for which adsorption data were already available with a view to determining what correlation might exist.

¹ Benton and White, *J. Am. Chem. Soc.*, **52**, 2325, 1930; Kingman and Garner, *Nature*, **126**, 352, 1930; *Trans. Faraday Soc.*, **27**, 1, 654, 1931; Taylor, *J. Am. Chem. Soc.*, **53**, 578, 1931; Taylor and Williamson, *J. Am. Chem. Soc.*, **53**, 813, 1931; Taylor and McKinney, *J. Am. Chem. Soc.*, **53**, 3604, 1931; Taylor and Hickman, *Nature*, 10th Oct., 1931; and forthcoming paper, *J. Am. Chem. Soc.*, 1932.

² *Z. physik. Chem.*, **4B**, 113, 1929.

Our data establish conclusively that the spin-isomerisation is not induced by van der Waals' adsorption but is always associated with activated adsorption of hydrogen, and is governed in its velocity of change by the extent and energy of activated adsorption at the pressure and temperature in question.

Experimental.

Apparatus and Experimental Method.—Our apparatus and experimental procedure were essentially those used by Bonhoeffer and Harteck. Electrolytic hydrogen carefully freed from oxygen and water vapour by passage over platinised asbestos and phosphorus pentoxide and through a liquid air trap was used in all the experiments. Studies were made of the capacity of surfaces to induce the change from normal (3 *ortho*- : 1 *para*-) hydrogen to "liquid air equilibrium" (1 *ortho*- : 1 *para*-) hydrogen at liquid air temperatures. At higher temperatures (-80° C. and upwards) studies were made of the capacity of surfaces to induce the reverse change from 1 : 1 to 3 : 1 since, from -80° C. upwards, the equilibrium hydrogen is substantially 3 *ortho* : 1 *para*. In such cases the 1 : 1 product was obtained by passing normal hydrogen over a well-out-gassed charcoal maintained at the temperature of liquid air.

The measurement of the extent of inter-conversion was made by the thermal conductivity method of Bonhoeffer and Harteck. The pressure of hydrogen in the thermal conducting vessel was always 40 mm. and the vessel was always maintained in liquid air during the measurements. The resistance of the fine platinum wire of the thermal conductivity cell after a given amount of current had been passed, gave a measure of the gaseous thermal conductivity, a Wheatstone bridge arrangement being employed for the resistance measurement. The heating current employed was 0.5 amperes from a constant battery source for a period of exactly one minute. The resistance thus obtained was calibrated with normal 3 : 1 hydrogen, with 1 : 1 hydrogen and mixtures of these gases. Since the thermal conductivity of *para*-hydrogen is greater than that of *ortho*-hydrogen a *para*-rich mixture conducts more heat from the wire to the walls in a given time than does an *ortho*-mixture, and hence the temperature and therefore the resistance of the wire will be less in the former case than in the latter.

The bridge reading for the hydrogen leaving the surface under study was normally intermediate between that for the 3 : 1 hydrogen and that for the 1 : 1 hydrogen. The percentage conversion or reversion, *i.e.*, the percentage approach to equilibrium, was assumed to be proportional to the bridge readings between 1 : 1 and 3 : 1 hydrogen. Actually Bonhoeffer and Harteck found the proportionality to exist between the resistances rather than the actual bridge values, but it can be shown that the former assumption is correct to well within our experimental error.*

* If x is the bridge reading corresponding to 1 : 1 hydrogen, y that for 3 : 1 hydrogen, and z that for the hydrogen under study, it was assumed that the fractional reversion was $(z - x)/(y - x)$. According to the results of Bonhoeffer and Harteck, the fractional reversion would be :

$$\frac{\frac{z}{1-x} - \frac{x}{1-x}}{\frac{y}{1-y} - \frac{x}{1-x}} = \frac{z-x}{y-x} \cdot \frac{1-y}{1-x} \text{ where } \frac{1-y}{1-x} \sim 1.$$

Experimental Results.

The complete experimental results with various surfaces at different temperatures and pressures are collected together in Table I. The first column gives the nature of the surface and the weight of sample taken. The second gives the operating temperature, 90° K. for the conversion of 3 : 1 to 1 : 1 hydrogen, 193° K. and upwards for the reverse process. The third and fourth columns give the percentage conversion efficiencies in the one or other direction. The fifth and sixth columns show the operating pressures and times of contact respectively. The data with respect to the methods of preparation of the materials and the significance of the numerical data will be discussed separately for each substance studied.

Nickel.—The active material was prepared from approximately 20 grams of a NiO-kieselguhr preparation. It was reduced *in situ* in hydrogen at temperatures which rose to 130° C. during the first four hours, rose further to 160° during the next hour, and were maintained there for fourteen hours. Finally, the sample was brought to 450° C. over a period of six hours and kept there for fourteen hours. It was then cooled in an atmosphere of the hydrogen. The sample was approximately 15 per cent. Ni. It was known, from previous work with this type of product as a catalytic material, to be a very highly active preparation.

The tabulated results show that it produces 1 : 1 hydrogen at liquid air temperatures at flow velocities of 100 c.c. per minute at a rate comparable with that of our charcoal. Rapid reconversion of 1 : 1 to 3 : 1 occurs also at room temperatures. This efficiency in producing *para*-hydrogen is in good accord with expectations from the adsorption data of Benton and White.¹ With a much inferior nickel preparation they showed that activated adsorption of hydrogen occurs on nickel at temperatures as low as -110° C. Our data show that with the more active preparation such adsorption occurs at liquid air temperatures. That the activity of the surface was the important factor is evident from the data with small wire fragments of nickel. With such, at 90° K., there was no measurable *para*-hydrogen formation. Bonhoeffer and Harteck's observation of the feeble activity of nickel in the reconversion process must likewise be attributed to the use of a preparation of small surface activity.

Zinc Oxide.—The sample was prepared by ignition for two hours at 400° C. of a sample of zinc oxalate prepared by precipitation of molal zinc nitrate with molal ammonium oxalate. It was then heated to 400° C., *in situ*, in an atmosphere of hydrogen, and then cooled.

Adsorption data by Taylor and Sickman¹ show such a preparation to have moderate van der Waals' adsorption for hydrogen at 90° K. and 193° K. From 0° C. upwards a slow activated adsorption sets in, readily measurable as to rate in the region 110° to 218° C. The conversion data in Table I. show that in spite of van der Waals' adsorption no *para*-hydrogen is formed at 90° K. From room temperatures upwards there is associated with the activated adsorption a reconversion efficiency which increases with temperature increase, with an activation of approximately 15 cal.

Zinc Chromium Oxide.—The sample was prepared by ignition for two hours at 400° C. of zinc ammonium chromate prepared by precipitating in the cold molal zinc nitrate with molal ammonium chromate

TABLE I.—ORTHO-PARA HYDROGEN CONVERSION AT VARIOUS SURFACES AT VARYING TEMPERATURES AND PRESSURES.

Nature of Surface and Weight of Sample.	Temperature (°K).	Ortho-Para Conversion (%)	Para-Ortho Re-conversion (%)	Pressure (cm.).	Time of Contact.	Nature of Surface and Weight of Sample.	Temperature (°K).	Ortho-Para Conversion (%)	Para-Ortho Re-conversion (%)	Pressure (cm.).	Time of Contact.
Ni, from oxide, 15 g.	90	100			Approx. 100 c.c./min.	CuO . Cr ₂ O ₃ 45 g.	273		55	20	5 min.
	298				50 "		273	100		20	15 "
		100			15 min						
		100		20							
Ni wire, small strips, 90 g.	90	0			Approx. 100 c.c./min.	Al ₂ O ₃ , circa 10 g.	298		0	20	15 min.
							373		0	20	"
							580		0.8	20	"
							674		14	20	"
							715		40	20	"
							760		98	20	"
							808	100		20	"
ZnO, ex. Oxalate, 15 g.	90	0			Approx. 100 c.c./min.	Charcoal, 20 g.	90	100			100 c.c./min.
	298				"		193		55	20	3.5 min.
	298	0			20 c.c./min.		193	100		20	15 "
	298				15 min.		217		29	20	3.5 min.
	322	1.4			"		237		13	20	"
	353	4.3			"		273		8	20	"
	373	36.4			"		298		4	20	"
		79.5			"		298		8	20	"
							298		0		15 min.
							298		0		30 "
ZnO . Cr ₂ O ₃ ex. chromate, 10 g.	90	0			15 min.		369	10	20		15 "
	90	0			14 hrs.		373	4	20		3.5 min.
	298	100			15 min.		273	6	10		"
							273	9	20		"
							273	16	35		"
							273	23	55		"
							273	34	76		"
							273	9	20		"
CdO, 41 g.	298	0	20		15 min.		273	13	20		5 min.
	320	0	20		"		273	24	20		10 "
	346	0	20		"		273	36	20		15 "
	373	0	20		"		273	40	20		20 "
							273	45	20		25 "
							273	47	20		30 "
Cd. 36 g.	298	0	20		15 min.		273	25	40		5 "
	373	0	20		"		273	43	40		10 "
	525	0	20		"		273	50	40		15 "
	574	35	20		"						
MnO . Cr ₂ O ₃ 15 g.	90	0			15 min.						
	193	0			5 "						
	193	0			10 "						
	193	0			15 "						
	273	17	20		5 "						
	273	61	20		10 "						
	273	81			15 "						
	285	68	20		5 "						
	296	100	20		5 "						

the solution being brought to neutrality by addition of ammonia. About 10 grams of product were reduced to a gray green mass in hydrogen, *in situ*, at 400° C. for four hours, and then cooled in hydrogen.

Adsorption data on such preparations show high van der Waals' adsorption at 90° and 193° K. At 0° C. and upwards there is an energetic adsorption of activated hydrogen at velocities much greater than in the case of zinc oxide just considered. The conversion data are consistent with this. At 90° K. there is no *para*-hydrogen formation even after fourteen hours' contact. At 298° K. the reconversion is 100 per cent. complete under conditions where with zinc oxide the reconversion was just barely manifesting itself.

Cadmium and Cadmium Oxide.—The oxide was prepared by ignition at 325° C. of a precipitated oxalate. The cadmium was then prepared by reduction of such oxide at 250° C. for sixteen hours and then at 300° C. for eighteen hours. Neither sample showed conversion or reconversion efficiencies even up to temperatures of 250° C. At 300° C. the metal showed a 35 per cent. reconversion. The marked contrast between these and zinc oxide is worthy of further study.

Manganous Chromium Oxide.—This was part of the actual sample described and used by Taylor and Williamson¹ in their adsorption studies. In spite of its known van der Waals' adsorption of hydrogen at 90° K. and 193° K. there is no tendency to produce or reconvert *para*-hydrogen at these temperatures. The existence of activated adsorption from 0° C. upwards is paralleled by the reconversion efficiency which increases with temperature the activation energy being approximately 19 Kg. Cals. The magnitude of this energy is in accord with the concept that the activated adsorption and desorption is the rate determining factor, not the van der Waals' process for which the heat of adsorption was found to be only 1.9 Kg. Cals.

Copper Oxide—Chromium Oxide.—This sample was prepared as in the case of zinc chromium oxide but was heated and reduced in hydrogen at temperatures not exceeding 350° C. It showed good reconversion efficiencies at 273° K., at which temperature activated adsorption of hydrogen is first becoming measurable in rate (unpublished data by Taylor).

Alumina.—This, a typical dehydration catalyst with negligible dehydrogenation activity, was prepared by precipitation of aluminium hydroxide from a solution of the pure nitrate by means of ammonia. The washed hydroxide was dried at 110° C. and slowly raised in temperature to 400° C. in an atmosphere of hydrogen. As will be observed in Table I. such material has no *para*-hydrogen conversion efficiency until a temperature greater than 300° C. is reached. At 400° C. the conversion efficiency is only 14 per cent. with fifteen minutes' contact time. This result is in accord with the adsorption studies by Taylor² on the same material, it being there shown that between 0° C. and 400° C. there is negligible adsorption of hydrogen. Above 400° C. a slow activated adsorption of hydrogen occurs. The high temperature coefficient of conversion (activation energy about 25 Kg. Cals.) is in accord with the high activation energy of adsorption found by Taylor in this case.

Charcoal.—The charcoal used in these experiments was a sample of German char left by Bonhoeffer in the Princeton laboratories. Its ash content is unknown, but the char is characterised by its rapid

² Z. physik. Chem., Bodenstein Festband, 475, 1931.

efficiency in *para*-hydrogen formation at liquid air temperatures. The principal object of our work with this agent was to investigate the reasons for the decreasing efficiency of reconversion to 3 : 1 hydrogen as the temperature was raised. The first data in the charcoal section show this at once. With a contact time of 3.5 minutes the percentage reconversions at a pressure of 20 cm. and temperatures of 193°, 217°, 237°, 273° and 298° K. are, respectively, 55, 29, 13, 8 and 4 per cent. The cause for this highly interesting decreasing velocity of surface reaction with increasing temperature is evident from the final figures in Table I. for the rate of reaction at 273° K., with pressures of 20 and 40 cm. respectively. It is evident from these that the half-life of the *para*-hydrogen is inversely proportional to the pressure employed, the well-known characteristic of a bimolecular reaction. Since hydrogen adsorption on charcoal at these temperatures is exceedingly small, and so obeys Henry's Law approximately, one must conclude that the surface process is also a bimolecular process. On this basis, the decreased reaction velocity with increase of temperature must be ascribed to the decreased adsorption with increasing temperature effecting a corresponding decrease in the probability that the two molecules will be found adsorbed on the surface sufficiently adjacent to one another that interaction may occur.

Decrease in surface reaction velocity of surface bimolecular reactions with increase of temperature due to this cause are to be expected not only in this type of change but also in true chemical reactions. They appear hitherto to have escaped record. Pease,⁴ in his study of the hydrogen ethylene reaction on poor copper catalysts at 200°-250° C. observed temperature effects which may in part have been due to this. The matter is now receiving special study. From the preliminary results with copper obtained by reduction of the oxide and heat-treated at 250° C., it is evident that the same phenomenon obtains with the *para*-hydrogen reconversion on copper as on carbon but in higher temperature ranges. From 193° to 423° K. a reduced copper showed a 100 per cent. reconversion efficiency; above this temperature of 423° K. the efficiency for a given contact time showed a decrease with increasing temperature paralleling that observed above with charcoal in the range 193° to 273° K.

Our knowledge of hydrogen adsorptions on copper in this temperature interval ($> 423^{\circ}$ K.) indicates that the cause of the decrease is the same as in the charcoal case.

It is also of interest to record that even our most active copper preparations are consistently inferior to those of nickel in the conversion of normal to 1 : 1 hydrogen at liquid air temperatures. This points definitely to a superior efficiency of nickel in activating hydrogen for adsorption, in other words a lower energy of activation of adsorption for nickel than for copper.

General Conclusion.

The experimental evidence shows decisively the parallelism between the capacity of surfaces to show activated adsorption of hydrogen and their capacity to induce the spin-isomerisation of hydrogen. No such relationship exists between van der Waals' adsorption of hydrogen on surfaces and *para*-hydrogen conversion. Consequently it seems desirable to make use of the *para*-hydrogen changes on surfaces as an index

⁴ *J. Am. Chem. Soc.*, **45**, 2235, 1923.

of the nature of the adsorption process occurring with hydrogen at surfaces. Furthermore, the same process can be utilised as a definite criterion of the capacity of surfaces for activating hydrogen for the numerous processes of hydrogenation and reduction in which the use of such surfaces may be contemplated. It thus becomes a tool for use in catalytic work.

Summary.

1. Surfaces at which activated adsorption of hydrogen occurs show a parallel efficiency in effecting *ortho-para*-hydrogen interconversion.
2. No such parallelism exists between van der Waals' adsorption and the interconversion process.
3. Nickel, zinc oxide, zinc-chromium oxide, manganous-chromium oxide, copper-chromium oxide, and alumina have been used for this purpose.
4. Charcoal shows a decreasing efficiency in converting *para-* to *ortho*-hydrogen with increasing temperature. This has been shown to be due to the bimolecular nature of the surface process which decreases due to increasing bareness of surface with increase of temperature.

*Frick Chemical Laboratory,
Princeton, N.J.*

THE KINETICS OF THE ADSORPTION OF HYDROGEN ON PLATINUM AND NICKEL.

BY E. B. MAXTED AND N. J. HASSID.

Received 21st December, 1931.

The total process involved during the adsorption of hydrogen on metals such as platinum or nickel may apparently be resolved into at least two definite components, namely into an exceedingly rapid primary adsorption and a far slower secondary process.

With regard to the nature of these two components two main views exist. According to the first of these, the primary process is one of true adsorption, while the slower component is regarded as being due to the gradual penetration, by diffusion or solution, of the gas into the interior of the metal. A second interpretation¹ involves the postulation of two true adsorption processes, associated, respectively, with the adsorption of hydrogen in the molecular and in the atomic form, and with a higher activation energy for the slower than for the rapid component.

While the variation, with temperature and pressure, of the total adsorption of hydrogen on metals has been investigated in considerable detail,² relatively few figures have been published with regard to the relative magnitudes of the fast and of the slow components at various temperatures and to the general kinetics of these components. It was considered therefore that a study of the adsorption process from the

¹ Taylor, *J. Amer. Chem. Soc.*, **53**, 578, 1931.

² Von Hemptinne, *Z. physikal. Chem.*, **27**, 429, 1898; Taylor and Burns, *J. Amer. Chem. Soc.*, **43**, 1273, 1921; Gauger and Taylor, *ibid.*, **45**, 926, 1923; Nikitin, *Z. anorg. Chem.*, **154**, 130, 1926; *J. Russ. Phys.-Chem. Soc.*, **58**, 1081, 1926; Benton and White, *J. Amer. Chem. Soc.*, **52**, 2325, 1930.

above standpoint should yield data which would be of special interest in the interpretation of the probable nature and mechanism of the component processes.

Experimental.

The apparatus employed consisted of a small adsorption pipette, containing the platinum or nickel and sealed by means of capillary tubing to a measuring system made up of a larger and of a smaller gas burette immersed in a thermostat. This adsorption pipette could be heated or cooled to the temperature required for the measurement by means of a suitable bath.

In order to render more accurate the volume correction for temperatures widely removed from that of the laboratory, a compensating bulb, containing hydrogen and having a capacity approximately equal to the dead space in the adsorption pipette, was mounted side by side with this in the heating or cooling bath, the change in apparent volume being measured on a further gas burette, which was placed in the thermostat together with the main gas burettes.

The platinum was prepared by the reduction of chloroplatinic acid with an alkaline formate solution. The nickel was obtained by converting nickel nitrate, by gentle ignition, to the black oxide, which was reduced by hydrogen at a temperature not exceeding 300°, and transferred to the adsorption pipette in an atmosphere of nitrogen. Calibration of all volumes was carried out with helium. For degassing between adsorption measurements, a pump of Töpler type was used, the platinum being degassed, unless mentioned specially, at 100°, and the nickel at 250°.

Table I. contains the results of a series of measurements with platinum at various temperatures, the total adsorption being resolved, by extra-

TABLE I.

Pt = 7.85 g.

Temperature °C.	Hydrogen Adsorption in c.c.		
	Primary.	Secondary.	Total.
-190	6.90	0.31	7.21
	6.88	0.32	7.20
-79	6.12	1.00	7.12
	5.90	0.98	6.88
0	5.33	1.58	6.91
50	5.00	0.80	5.80
100	4.40	0.0	4.40

polation of the adsorption-time curves, into primary and secondary adsorption. The secondary adsorption represents the additional hydrogen adsorbed during the first three hours after admission of hydrogen, this period being necessary for the approximate attainment of equilibrium. All gas volumes are reduced to N.T.P., and all adsorptions were made at atmospheric pressure.

While the plotting merely of the total adsorption against the temperature leads to a curve of no special suggestiveness, an interesting relationship is obtained on plotting the primary and secondary components separately. This has been done in Fig. 1, from which it will be seen that the primary adsorption decreased approximately linearly with increasing temperature. The secondary adsorption, on the other hand, rose from a low value to a maximum, and sank to zero once more as the temperature of degassing was approached. It may be noted that Taylor and Burns² found that the total adsorption of hydrogen by

platinum was less at 110° than at 25° , in qualitative agreement with the above results for the total adsorption.

In order to show the sharp distinction between the rapid primary phase and the far slower process of secondary adsorption, several

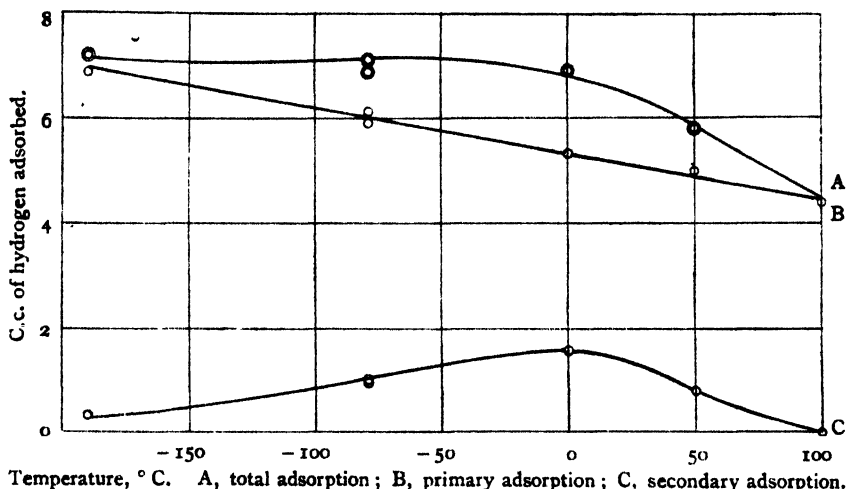


FIG. 1.—The kinetics of the adsorption of hydrogen on platinum and nickel.

typical complete adsorption-time curves have been plotted in Fig. 2. In view of the relative smallness of the secondary adsorption with platinum compared with the limits of accuracy of the apparatus and the largeness ($0.2-0.3$ c.c.) of the correction for thermal expansion due to

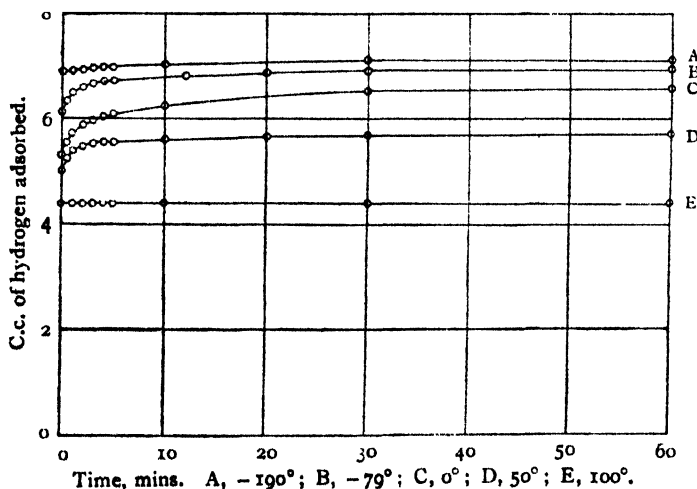


FIG. 2.—The kinetics of the adsorption of hydrogen on platinum and nickel.

adsorption heat, no attempt has been made to analyse the kinetics of this secondary adsorption; although this was done for nickel, for which the secondary adsorption, under certain conditions, is larger and the expansion correction less.

The sinking of the secondary adsorption to zero at the temperature (100°) used for degassing between adsorption measurements suggested a trial of the effect of a higher degassing temperature. This was done after the completion of the series, since, in the carrying out of a normal series of measurements, a relatively low degassing temperature was used in order to avoid, as far as possible, structural alterations in the platinum. On raising the degassing temperature from 100° to 150° , the secondary adsorption at 100° rose from zero to 0.50; and, for an adsorption at 150° , the secondary adsorption was now zero. It would thus seem that the secondary adsorption is a function of the temperature used for degassing, and vanishes when the adsorption temperature and the degassing temperature are equal.

In the case of nickel, a complicating factor, which is absent with platinum, is involved. Nickel catalysts reduced at moderate temperatures necessarily contain some unreduced oxide, which, unless reduction has been pushed sufficiently far by employing a specially long time of reduction, reacts with part of the adsorbed hydrogen during the process of degassing at 250° . This further reduction is indicated by a disturbance of the hydrogen balance, in that less hydrogen is pumped off as such than was adsorbed.

After a considerable amount of work had been carried out, it became evident that the surface changes brought about by this slow additional reduction were responsible for irregular results; and it was found that consistent values were obtained most readily with nickel which had been reduced until a stage had been reached at which no further reduction took place during degassing. This nickel exhibited considerably less secondary adsorption, for instance at 0° or even at -80° , than a less completely reduced nickel; and, at these low temperatures, the difference cannot be due to reduction.

With the nickel employed for the following measurements, the volume of hydrogen pumped off after an adsorption corresponded with that adsorbed within a limit of 0.2 c.c., save that in one adsorption measurement at 250° , 0.35 c.c. of hydrogen was lost during adsorption and degassing. The total adsorption is of the order of 3.4 c.c. so that the form of the curves is not effected by losses or apparent gains of the above small

TABLE II.

$Ni = 7.0 \text{ g.}$

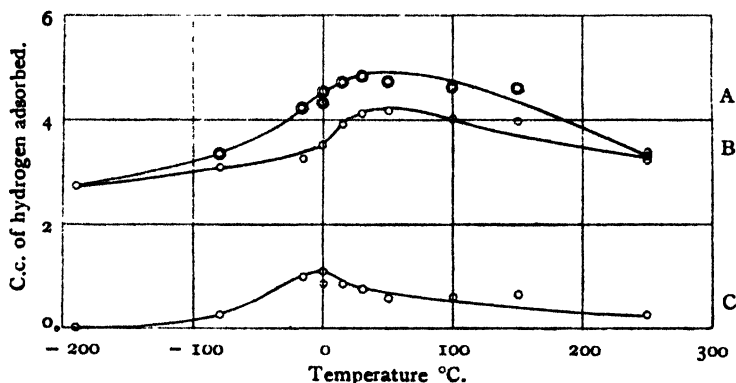
Temperature $^{\circ}\text{C}$	Hydrogen Adsorption in c.c.		
	Primary.	Secondary.	Total.
-190	2.72	0	2.72
-79	3.10	0.24	3.34
-15	3.26	0.96	4.22
0	3.51	0.82	4.33
0	3.50	1.05	4.55
15	3.91	0.83	4.74
30	4.11	0.73	4.84
50	4.17	0.55	4.72
100	4.02	0.59	4.61
150	3.99	0.62	4.61
250	3.24	0.23	3.47
250	3.31	0.18	3.49
250	3.35	0.23	3.58

order of magnitude; and the constancy of the surface condition is shown by the approximate correspondence of the duplicate measurements at 0° and 250° , which were carried out at wide intervals in the series of tests. The relative values of the primary and secondary adsorption at various temperatures are shown in Table II. The secondary adsorption was in this case only measured for the first thirty minutes after admission of the gas.

These results are shown graphically in Fig. 3. It will

be seen that, while the form of the secondary adsorption curve agrees with that found for platinum, the primary adsorption rises to a maximum value for about 50° and subsequently sinks with increasing temperature. The form of the total adsorption curve may be compared with that obtained by Benton and White, with which it is somewhat similar, save that the maximum observed by these authors occurred in the neighbourhood of -100° . The temperature range was, in the present work, not extended below liquid air temperature in order to confirm Benton and White's observation of the greatly increased total adsorption at temperatures in the neighbourhood of -200° , save that no sign of this was noted at -190° .

The primary adsorption of hydrogen involves too great a reaction rate to be followed by ordinary means; but, in view of the relatively large secondary adsorption exhibited by specimens of nickel which have not been stabilised by excessive heat treatment—carried out in hydrogen



A, Total Adsorption; B, Primary Adsorption; C Secondary Adsorption.
FIG. 3.—The kinetics of the adsorption of hydrogen on platinum and nickel.

at 300° , with the view of removing oxide—an attempt was made to analyse the kinetics of this latter component.

The reaction path was apparently approximately of the first order, at any rate until the bulk of the hydrogen had been absorbed, but the agreement was not complete; and, in all the curves analysed, there was a consistent tendency towards the falling off in the first order reaction constant at advanced stages of the adsorption. The possible correction for thermal expansion due to adsorption heat is of the order of 0.1 c.c. only; and the reason for the slight but persistent deviation from the simple logarithmic course apparently lies in the process itself.

The degree of agreement with the first order curve in the case of two typical adsorptions with 5.8g. of nickel at 0° —at which temperature the secondary adsorption is large—is shown in Table III. The agreement in the value of the reaction constants from experiment to experiment will be noted. The constants fall off appreciably at stages corresponding with more than about two-thirds of the total secondary adsorption, namely, after the first five to ten minutes under the above conditions. The falling off is also illustrated by the results of the fifth column, which have been calculated by means of the relationship, $v = a(1 - e^{-kt})$, a value of 0.15 being taken for k .

TABLE III.

Temperature of Adsorption, °C.	Time, Mins.	Secondary Adsorption (Observed), c.c.	k_1 .	Secondary Adsorption (Calculated), c.c.
0	1	0.70	0.15	0.69
	2	1.29	0.15	1.28
	3	1.79	0.15	1.79
	4	2.21	0.15	2.22
	5	2.51	0.14	2.60
	10	3.32	0.11	3.88
0	1	0.64	0.15	0.62
	2	1.23	0.16	1.16
	3	1.70	0.16	1.62
	4	2.07	0.15	2.03
	5	2.42	0.15	2.36
	10	3.30	0.13	3.48

It should be noted that a logarithmic curve would be expected both from a process of the solution or penetration type and from a true adsorption, provided that the latter process follows Langmuir's conception; for, if N and n represent, respectively, the total effective number of elementary adsorbing spaces and the number occupied at a given time by hydrogen, and v the volume of hydrogen adsorbed, then the speed of adsorption will be given by the relationship

$$\frac{dv}{dt} = k_1(N - n) - k_2n$$

which is equivalent to

$$\frac{dv}{dt} = \text{Const.} - v.$$

In view of the similarity in reaction path of a true adsorption and of a penetration process, the value of the activation energy, also the magnitude and variation with temperature of the rate of passage of hydrogen through a thin platinum or nickel diaphragm, are of considerable interest. In the present case, however, the critical increment appears not to be obtainable from the observed temperature coefficient without applying a correction for the evident operation of factors other than temperature—for instance the influence of the temperature of degassing—on the reaction rate, whereby the apparent temperature coefficient may even have a negative value. Thus, the first order reaction constant sank from 0.15 to about 0.09 on raising the adsorption temperature from 0° to 100° with the nickel used for Table III.; and, although with certain specimens of nickel the apparent temperature coefficient, for temperatures in the neighbourhood of 0°, rose to a value of 1.4 for a 10° rise, the figures, apart from the presence of disturbing factors, are based on too small volume measurements to justify any calculation of the critical increment; and further work with larger quantities of metal is needed. It may be noted that Taylor³ has calculated an activation energy of 14,000 cal. for the slow adsorption of hydrogen on zinc oxide at temperatures above 0°, evidence being also adduced for the existence, at low temperatures, of a further type of adsorption, associated with no activation energy.

³ *Nature*, 128, 636, 1931.

If energy relationships are introduced into the fundamental Langmuir equation given above, it should be possible to obtain an expression connecting the adsorption rate with the temperature. Considering, for the sake of simplicity, a single type only of adsorption, then, if the adsorption of hydrogen by a bare surface element, on the one hand, or the breaking up of a metal-hydrogen complex, on the other, be dependent on the attainment by this element of a minimum energy E_1 and E_2 , respectively,

$$\frac{dv}{dt} = k_1(N - n)e^{-E_1/RT} - k_2ne^{-E_2/RT}.$$

In practice, the hydrogen value of N is difficult to determine; although the metal may be completely degassed at the end of a series of measurements by employing a high degassing temperature, whereby the normal adsorbing surface is destroyed; but n can be more nearly identified with v by introducing the expression $a + v$ in place of n , a being the volume of hydrogen left in the metal after degassing and v the volume adsorbed after time t .

The expression thus becomes

$$\frac{dv}{dt} = k_1(N - a - v)e^{-E_1/RT} - k_2(a + v)e^{-E_2/RT}$$

which gives the influence, on the above basis, of the temperature on the secondary adsorption and which reduces to a simple first order reaction path for a constant temperature. The limit of adsorption is the stage at which the two terms on the right of the above equation become equal; and, if the conditions of temperature and pressure are changed such that the latter of these two terms becomes greater than the first, desorption takes place.

The value of a is considerable, since a metal such as platinum is by no means completely degassed even by efficient evacuation at 100° . The following volumes, for instance, of gas were evolved on evacuating, at successively higher temperatures, 7.85 g. of platinum black, previously degassed at 100° .

TABLE IV.

Temperature of Evacuation, °C.	Additional Volume of Hydrogen Evolved, c.c.
150	3.60
250	3.91
350	4.18
	Total: 11.69

Finally, while it is not proposed in the present paper to discuss the evidence for adsorption components of differing activation energies, it would appear not to be impossible that the rapid primary adsorption phase might be induced, even in an adsorption process associated with a single activation energy only, by the abnormal conditions which exist on the surface during the period preceding the establishment of normal kinetic exchange, namely by the operation of the heat of adsorption—under the preliminary conditions during which this is not thermally neutralised by desorption—as a source of activation energy for primary

adsorption; secondary adsorption, on the other hand, like desorption, being dependent on the attainment of sufficient energy in the course of the continuous rearrangement of the energy distribution within the surface. The quantitative application of this to the observed variation of primary adsorption with temperature involves a knowledge, not only of the magnitude of E_1 and Q , but also of the variation of these with temperature, particularly since it is only at the temperature used for degassing, or at very low temperatures—at which the probability of the attainment of sufficient energy by a surface element during the normal state which follows primary adsorption is low—that the whole of the adsorption takes place practically instantaneously.

It may be noted that, while the most obvious conception of primary adsorption is as a distinct process of low activation energy, it is difficult, if this is the case, to see why primary adsorption should be affected so markedly by the presence of even small quantities of a poison.⁴

Effect of the Temperature of Admission of the Gas on the Total Adsorption.

It is well known that, if the temperature at which hydrogen is admitted to a previously degassed metal does not coincide with that at which the adsorption measurement is made, different values are obtained for the volume adsorbed than is the case if the adsorption temperature and the temperature of admission of hydrogen are the same.⁵

The effect was therefore tried of admitting hydrogen at 250° to the nickel used for the results of Table II., this nickel having been previously degassed at 250°, and allowing the system to remain at various successively lower temperatures for a sufficient time for the attainment of approximate equilibrium at the temperature in question. The results of measurements made in this way are given in Table V., the normal adsorptions—namely the adsorptions observed when the gas is admitted at the adsorption temperature—being also included for purposes of comparison.

TABLE V.—HYDROGEN ADMITTED AT 250°.

Adsorption Temperature, °C.	Total Hydrogen Adsorption, c.c.	Total Normal Adsorption, c.c.
250	3.6	3.58
150	5.0	4.61
100	5.32	4.61
50	5.65	4.72
0	6.19	4.55
— 79	6.54	3.34
—190	8.50	2.72

It will be seen that the increase in the hydrogen adsorption, compared with its normal value, caused by admitting the gas at a higher temperature, becomes greater as the adsorption temperature becomes more widely removed from the admission temperature, and is thus, under the above conditions, especially marked for low adsorption temperatures.

⁴ *J. Chem. Soc.*, 2203, 1931.

⁵ See, for instance, Benton and White, *loc. cit.*

An additional adsorption at a given temperature is also caused by raising the temperature of the system to a higher value, without degassing, and afterwards cooling to the original temperature. The additional adsorption is, as before, increased by increasing the temperature range through which the system is heated and cooled; but a repetition of the heating and cooling between two given temperatures does not increase the adsorptive power at the lower temperature beyond a certain limiting value. This is illustrated in Table VI., for which the same specimen of nickel was used as for the previous Table. This was degassed at 250°, hydrogen being subsequently admitted at -79°. It was then successively brought to the series of temperatures given in the table, and allowed to remain at the temperature in question until no appreciable further adsorption was observed. The adsorption was completely reversible, the total volume of hydrogen adsorbed being removed, after completion of the series, by degassing once more at 250°.

The additional adsorption caused by previous exposure to a higher temperature would appear to be due to some form of energetic activation. The occurrence of a maximum value for the increase caused by a given temperature change, followed by the return to the original temperature, is of considerable interest and will be discussed in greater detail in a later paper.

*Department of Physical Chemistry,
University of Bristol.*

TABLE VI.

Temperature, in Sequence, °C.	Total Hydrogen Adsorption, c.c.
-79	3.30
0	4.71
-79	5.13
0	4.81
-79	5.23
0	4.81
-79	5.23
0	4.81
100	4.78
0	5.74
100	4.98
0	5.74
-79	6.16
0	5.74
100	4.98
0	5.74
-79	6.16
-190	7.98
-79	6.24
-190	7.98

THE HEATS OF ADSORPTION AND THE KINETICS OF ADSORPTION.

BY W. E. GARNER.

Received 4th December, 1931.

The Heat of Adsorption.

During an adsorption process the energy levels of the adsorbed molecules and of the atoms composing the surface undergo modification, and also, as in most physical and chemical processes, there is a residuum of energy which is liberated as heat. The latter is called the heat of adsorption. This heat is the algebraic sum of the various energy changes occurring during the adjustment of the surface and molecular fields, and hence it is not possible to deduce from it the actual values of the changes in potential energy which take place at the surface. Nevertheless, there seems to be some correspondence between the magnitudes

of the heat of adsorption and of the potential energy changes. This correspondence is sufficiently exact to enable us roughly to classify adsorption processes by its aid.

Such a classification is possible because the energies associated with the rotational, vibrational and electronic levels of molecules respectively are of widely different magnitudes. At low temperatures, only changes in rotational levels and the kinetic energies of the molecules would be expected to occur on adsorption. Thus, at such temperatures, the potential energy changes and also the heat of adsorption must be small

in magnitude. As the temperature is raised, there successively appear changes in the vibrational and electronic levels, and since the rotational, vibrational-rotational, and the electronic-vibrational-rotational levels are usually widely separated on the energy scale, there must occur on raising the temperature discontinuous changes in the magnitude of the residuum of energy which is liberated as heat.

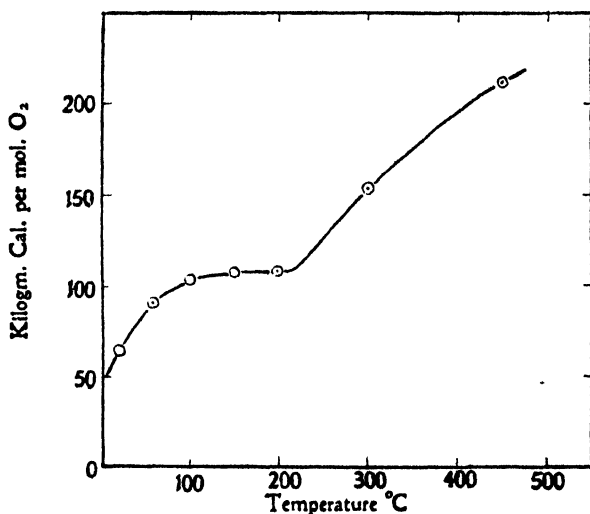


FIG. 1.—Heat of adsorption. Oxygen on charcoal.

Systematic measurements of the heats of adsorption have very rarely been made over a wide range of temperatures. The experimental data which are available have either been calculated by the application of thermodynamics to the adsorption isobar for a narrow range of temperatures or else have been measured experimentally for temperatures in the neighbourhood of 0° C. Sufficient has, however, been done for us to observe the trend of the values of the heat of adsorption with increase in temperature. That discontinuities do occur is abundantly evident from the work of H. S. Taylor on activated adsorption on many surfaces. Also, measurements of the heats of adsorption of oxygen on charcoal between 20° C. and 350° C. provide clear evidence for the same view (Fig. 1).

Adsorption at Low Temperatures.

When adsorption occurs at low temperatures, the heats of adsorption are not very much greater in magnitude than the kinetic energies of the adsorbed molecules. Thus, for the permanent gases adsorbed on mica at temperatures between -180° C. and -80° C., the heats of adsorption¹ range between 500-2000 calories pro mol. Also, the heat of adsorption of hydrogen on metals at these temperatures is of the same order.² These small heats of adsorption may be taken to indicate

¹ Langmuir, *J.A.C.S.*, **40**, 1361, 1918; Bawn, *J.A.C.S.*, **54**, 72, 1932.

² Benton and White, *J.A.C.S.*, **53**, 3301, 1931.

that the changes in potential energy which occur during adsorption are small in magnitude, and this is supported by the fact that the gases adsorbed under these conditions are not specially active chemically. The heats of adsorption are of the same order as those to be expected from the magnitude of the van der Waals' forces between the normal surface atoms and normal adsorbed molecules.³

Adsorption at Room Temperatures.

Since the heat of adsorption includes some of the energy of translation, rotation, etc., of the adsorbed molecule, it would be expected that it would increase with rise in temperature. This is found to be the case. Gases like nitrogen and ammonia adsorbed on charcoal at room temperatures give heats of adsorption of 4000-8000 calories.⁴ The heats of adsorption at room temperatures are sometimes found to depend on the number of gas molecules adsorbed per unit area of surface.⁵ For small amounts adsorbed, quite high values may be obtained. Thus, the differential heats of adsorption of oxygen on charcoal range between 90 in the initial stages of the adsorption to 4 cal. in the neighbourhood of saturation.⁶ The occurrence of such large energy changes demonstrates the occurrence of large changes in the potential energies of the surface atoms and of the adsorbed molecules. These are of such a magnitude that it may be that they are a consequence of chemical combination of the adsorbed molecule with the surface.

The processes which give rise to abnormally high heats of adsorption may be classified into two main groups, (1) reversible changes and (2) irreversible changes. In the first class, the adsorbed molecules can be recovered on desorption in an unchanged state, and in the second, desorption results in the volatilisation of some of the surface atoms in chemical combination with the adsorbed gas.

Reversible Adsorption at Moderate and High Temperatures.

The adsorption of hydrogen or carbon monoxide on metals and metallic oxides is in the majority of cases reversible at room temperatures, and the heats of adsorption lie between 10,000-30,000 cal./mol., whereas at lower temperatures the heats obtained with the same substances are of the order 1000-2000 calories. There is a complete change in the character of the adsorption process as the temperature is increased, for the adsorption isobar shows a minimum in several cases.⁷

Heats of adsorption of 30,000 cal. are of too large a magnitude to be due to the changes in potential energy which arise under the influence of the normal van der Waals' forces. Besides, these high temperature adsorption processes possess quite large critical increments.⁸

Benton and White² refer to these reversible adsorption processes as chemisorption, but H. S. Taylor leaves the question of their nature

³ Lennard-Jones and Dent, *Trans. Far. Soc.*, **24**, 92, 1928.

⁴ Cf. Hückel, *Adsorption und Kapillarkondensation*, p. 34.

⁵ This does not happen in many cases. In the adsorption of gases on metals, for example, the heat of adsorption is independent of the surface covered. Cf. Ward, *Proc. Roy. Soc.*, **133A**, 506, 1931, and Maxted and Hassid, *J.C.S. In press*.

⁶ Garner and Blench, *J.C.S.*, **125**, 1288, 1924; Garner and McKie, *J.C.S.*, **2451**, 1927; Keyes and Marshall, *J.A.C.S.*, **49**, 156, 1927.

⁷ Benton and White, *J.A.C.S.*, **52**, 2325, 1930; Taylor and Williamson, *J.A.C.S.*, **53**, 2168, 1931; Taylor and McKinney, *J.A.C.S.*, **53**, 3604, 1931.

⁸ Cf. H. S. Taylor, *J.A.C.S.*, **53**, 578, 1931.

more open by describing them as "activated" adsorption. This term "activated" is used to indicate that they possess a temperature coefficient, but it might also have been used to mean that the adsorbed molecules were in an active state. The latter seems to be true, for activated adsorption occurs at those temperatures for which the surface is catalytically active.⁸ In view of the fact that these processes possess a critical increment it is reasonable to refer to them as reversible activated adsorption.

The work of Ward⁸ on the adsorption of hydrogen on copper leads him to suggest that the slow reversible adsorption is due to lattice or intergranular diffusion. The heats of adsorption are so high that the adsorption process cannot be of the van der Waals' type. They are independent of the area of surface covered, which appears to conflict with the variable chemical activity of the surface atoms. Similar results have recently been obtained by Maxted.⁹ The theory that the rate of activated adsorption is actually governed by the rate of diffusion presents difficulties in that it does not explain the high temperature coefficient of the process, for diffusion processes normally increase as \sqrt{T} . If the slowness of the rate be due to diffusion, it follows that the diffusion must be of an activated type. (See later.)

Irreversible Adsorption.

The adsorption of oxygen on tungsten and of oxygen on charcoal are of this type, for on desorption, oxides of tungsten and carbon are liberated. Very few heats of adsorption have been measured in this class. For oxygen on charcoal, the heats are 70-200 cal./mol. oxygen adsorbed;⁶ and for oxygen on tungsten, 160 cal.¹⁰ These heats are much larger than those for reversible adsorption but this may be accidental, for irreversible chemical change does not necessarily take place with a very large heat of reaction. Gases adsorbed on surfaces irreversibly do not appear to be chemically reactive, in contradistinction to the reversible adsorption on metals and oxides. For example, hydrogen which is not appreciably adsorbed on carbon at room temperatures will not react with adsorbed oxygen nor is any water formed if oxygen and hydrogen are admitted simultaneously to the carbon.

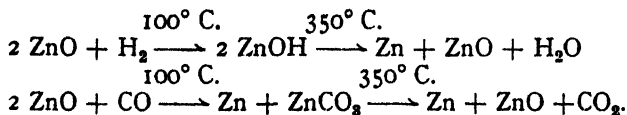
The transition from reversible to irreversible chemisorption has been observed in the case of hydrogen and carbon monoxide¹¹ on $\text{ZnO}-\text{Cr}_2\text{O}_3$ at 90° to 180° C. The heats of adsorption of these gases at room temperatures are 20-30 cal.; the values for the adsorption above the transition temperature have not yet been determined. If hydrogen or carbon monoxide is adsorbed on $\text{ZnO}-\text{Cr}_2\text{O}_3$ at room temperature at a pressure of 10^{-3} to 10^{-4} cm., and the temperature is rapidly raised to 90° to 180° C., the adsorbed hydrogen or carbon monoxide is desorbed unchanged. The pressure of the gas rises rapidly to a maximum, and then falls more slowly to zero, due to subsequent readorption (Fig. 2) After the second adsorption, the gases can only be removed from the surface on raising the temperature to 350° C. and then the gaseous products consist of water and carbon dioxide respectively. On desorption, oxygen atoms are removed from the surface at the same time as the adsorbed gas. The latter type of adsorption is thus an example of irre-

⁸ *J.S.C.*, 3313, 1931.

¹⁰ Langmuir and Kingdon, *Physic. Rev.*, 24, 570, 1924.

¹¹ Garner and Kingman, *Nature*, 126, 352, 1930; *Trans. Far. Soc.*, 27, 322, 1931.

versible chemi-sorption. The chemical change which results is very probably the combination of the gases with the oxygen on the surface to give OH and CO₂ groups. Thus,



If such be the case, then the process occurring at 20° C. cannot consist in the adsorption of hydrogen or carbon monoxide on the oxygen atoms of the catalyst. Kingman¹² has investigated the nature of the processes which occur during the adsorption of hydrogen on both the freshly-prepared and on the strongly reduced catalyst, and from the fact that the reversible type of adsorption increases in magnitude as the surface is reduced, concludes that the reversible adsorption occurs on the metal atoms. Thus, it is very probable that the "activated" reversible adsorption on metals and on oxides occurs on the same centres. There was also evidence in Kingman's work, that there are two different kinds of reduced centres on which the hydrogen is adsorbed, which in view of the complexity of the catalyst ZnO—Cr₂O₃ is what would be expected.

There have been distinguished at least three kinds of adsorption on oxide catalysts: (1) adsorption due to van der Waals' forces, (2) reversible chemi-sorption, and (3) irreversible chemi-sorption. It is of interest in this connection that Langmuir claims to have detected the existence of three types of adsorption of oxygen on tungsten.

The Rate of Adsorption.

The surfaces of catalytic substances resemble that of charcoal in that their main area is internal to the external surface of the grains composing the solid. A gas undergoing adsorption penetrates into the interior along passages the smallest of which may be of molecular size. Thus the rates at which a gas is adsorbed will depend partly on the rate of diffusion and partly on the true rate of adsorption, the latter being defined as the rate at which adsorption occurs on a plane surface directly accessible to the gas. Only when the rate of adsorption is much slower than the rate of diffusion will the rate of disappearance of the gas give

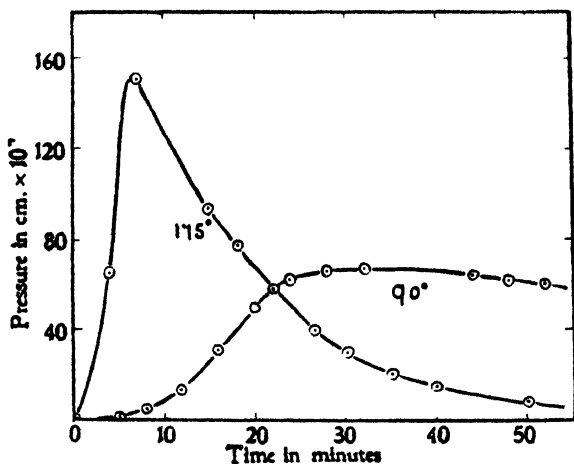


FIG. 2.—Desorption and readsorption of hydrogen on ZnO · Cr₂O₃.

the true rate of adsorption. Under these conditions, the pressure of the gas throughout the adsorbent will be in equilibrium with that in the free space.

There is no doubt that diffusion phenomena do determine the rate if the velocity of adsorption is very rapid. For example, the adsorption of small amounts of oxygen on a clean carbon surface is complete within two or three seconds and the whole of the adsorption is found to occur entirely on the grains forming the outside of the carbon mass.¹³ The rate of reaction is here much more rapid than the rate of diffusion. When the carbon is nearly saturated with oxygen, the rate of adsorption becomes measurable and proportional to the pressure. This is, however, what would be expected at low pressures, if the rate were determined by the rate of diffusion of oxygen through capillaries to the active carbon atoms on which reaction occurred, so that it cannot be concluded that even near saturation, diffusion effects are absent. Any measurements of rates are suspect until it has been definitely shown that diffusion effects are absent.

The recent work of Benton and White and of H. S. Taylor has, however, demonstrated that at low temperatures, adsorption of oxide and metal catalysts reaches equilibrium within a few minutes. If at low temperatures, gases can diffuse into the body of the catalyst and reach equilibrium in a very short time, it is clear that the diffusion effects of the same kind must be negligible at higher temperatures. It is, however, possible that at low temperatures the adsorption is limited to the external surface and the larger capillaries, and that at high temperatures, on account of increased molecular mobility on the surface, diffusion occurs into the intergranular spaces.

At very low temperatures, Benton and White find that adsorption is not instantaneous, although at higher temperatures it is so. Bawn, working in this laboratory, finds that although carbon monoxide at -78° reaches its equilibrium value on mica almost instantaneously, this is not the case at liquid air temperatures. At the latter, adsorption is not complete until after forty-five minutes. Since the heat of adsorption was quite small, the process which occurs is no doubt of the ordinary van der Waals' type, so that there is no question here of a critical increment for the process. The explanation of the result presents difficulties on the usual conception of the mode of action of the van der Waals' forces.

At moderate and high temperatures, the rates of adsorption usually observed often obey a very complex law. This is true for some of the oxide catalysts for which the rates of diffusion as measured at low temperatures are very rapid. In the initial stages of the adsorption, the rate of adsorption varies as a high power of the pressure, but in the final stages it often proceeds at a rate proportional to the square of the pressure.¹² Such complexities may be ascribed to a limited extent to the variation in the activity of the surface atoms of the adsorbent, but not entirely, for the first quantities of gas are often adsorbed on the outermost grains of the adsorbent.

In the case of the adsorption of hydrogen on carbon¹⁴ at $400-500^{\circ}\text{C.}$, conditions were found under which the critical increment of the process did not vary very greatly from the initial to the final stages of adsorption. These conditions were such that the amounts of gas employed were much

¹³ Bull, Hall and Garner, *J.C.S.*, 837, 1931.

¹⁴ Kingman, *This vol.*, 269.

smaller than those required for saturation. The critical increment of the process ranges from 27,500 to 31,000 calories and is practically constant after the first few minutes. Since, on desorption, hydrogen is the main product, the process belongs to the reversible class. It is thus suitable for the study of the kinetics of "activated" adsorption. It is found that the velocity of adsorption is given by

$$-\frac{dx}{dt} = ke^{-E/RT} \cdot p \cdot (N - N'),$$

where N is the number of carbon atoms which are available for the adsorption and N' is the number saturated with hydrogen at any time. N is not, however, constant, but practically doubles between 400-500° C. The critical increment of the increase in N is, however, very small compared with E , so that its neglect in the calculation of E by the method of Taylor and Williamson does not lead to appreciable error.

The above equation was derived on the assumption that diffusion effects do not enter into the rate of adsorption, and this is supported by the fact that it is possible to account for the changes in the rates of adsorption at constant temperature by an equation of the above type, in which the rate is given as proportional to the uncovered area of the carbon. On further consideration, however, the accuracy with which this equation fits the experimental results cannot be adduced, as was first thought, in proof of the absence of diffusion effects.

Activated Diffusion.

If activated adsorption occur on *activated* atoms which possess a life of the order of 10^{-13} second, so that the atom holding the adsorbed molecule is rapidly activated and deactivated, then it is possible to account for the independence of the heat of adsorption with the surface covered. If the rate of activation and deactivation of the surface atoms be independent of their chemical activity, then there will be no preponderance of adsorption on a few surface atoms of a special kind. The adsorption will be distributed equally over the whole surface.

Ward⁵ has shown that the rate of diffusion at constant temperature is proportional to the amount adsorbed on the readily accessible areas, not proportional to p , the pressure of the gas. The diffusion into the interior of the solid must therefore occur via the adsorption space, that is, within the sphere of action of the surface forces. This is what would be expected if the capillaries were of molecular size. Knudsen¹⁵ has shown that the rates of diffusion in capillaries of diameters less than the mean free path of the gas molecules obey another law than that obeyed at higher pressures, and he postulated surface flow in explanation of this fact.

The problem of activated diffusion thus resolves itself into a study of mechanism of surface flow. The concentration in the adsorption space at the outermost end of the capillary is proportional to the fraction of activated atoms, $e^{-E/RT}$, and to $p \cdot e^{Q/RT}$, where Q is the heat of adsorption. Thus, the surface concentration $= k \cdot p \cdot e^{(Q-E)/RT}$. The rate of flow along the capillary will be inversely proportional to the duration of time the molecules remain adsorbed at one spot, that is, to $e^{-D/RT}$. D and Q will normally cancel, so that the rate of diffusion will be proportional

to $e^{-E/RT}$, and the activation energy of diffusion becomes the energy of activation of the surface atoms.

The rate of diffusion will also be some function of $N - N'$ (see above), hence the results obtained for the activated adsorption of hydrogen on carbon cannot be taken to mean that diffusion effects are absent.

A summary of the data at present available on the heat of activated adsorption and the activation energy is given in the table. It will be

Gas.	Surface.	Heat of Adsorption. (Q . Cal.).	Heat of Activation. (E Cal.).
H ₂	Carbon	—	30
H ₂	Al ₂ O ₃	—	27.5
H ₂	Cu	33	14.1
H ₂	MnO	—	12—20
H ₂	MnO . Cr ₂ O ₃	20	6—10
CO	Pd	15	9

seen that E is less than Q in all cases for which data have been obtained. Since the activation energies vary with the surface, they cannot therefore consist in an electronic activation of the adsorbed molecule. There appear to be two possibilities, (1) that a hydrogen molecule becomes adsorbed on the surface when it collides with the surface atoms with kinetic energies equal to the above values; the additional energy required for activation is supplied by the surface atoms, or (2) it is the surface atoms which are activated. From the argument developed on p. 264, it will be seen that the latter is considered to be the more likely.

The Transition between the Various Types of Adsorption.

The isobars for hydrogen on nickel, on manganous oxide-chromic oxide, and on carbon, and of hydrogen and carbon oxide on zinc oxide-chromium oxide show a minimum at a temperature which varies with the chemical nature of the system investigated. There is thus a region of temperature over which adsorption increases with rise in temperature. In the case of reversible adsorption, the values for the adsorption in this region are reproducible as long as the temperature is not radically changed.² Taylor refers to the equilibria which are attained in the transitional regions as pseudo-equilibria. It is not clear what is meant by this term, for in no case is thermodynamic equilibrium ever attained.

The positive temperature coefficient in the transitional regions can be accounted for as follows. If E is the activation energy of the surface atoms and Q is the heat of adsorption, then the number of surface atoms N' which are activated $= N \cdot e^{-E/RT}$, where N is the total number of surface atoms, and the number of activated atoms which are covered with molecules of adsorbed gas will be $N'' = N \cdot e^{(Q-E)/RT} \cdot k \cdot p$. Over the transitional regions, $Q - E$ must first possess a negative value, which as the temperature increases becomes zero and then positive. The activation energy of the surface atoms is likely to increase with temperature, therefore Q must also increase. There are few data bearing on the change in Q with temperature, for the heats of adsorption are usually measured in a Bunsen ice calorimeter or else with a thermocouple calorimeter at room temperatures. In the case of the adsorption of oxygen on carbon, measurements are available above room temperatures.

The values increase from 70 to 110 cal. between 20° and 100° C., and then become practically constant for another 100° C. This is what would be expected of the heat of adsorption in the transitional regions.

The causes underlying increases of this type would possibly be different for the two types of transition, and there is perhaps little justification for speculation until the physical basis of reversible activated adsorption is better understood. It may, however, be mentioned that the number of times the surface atoms will be activated in unit time will increase with increase in temperature. Thus, the heat liberated on adsorption would be expected to be greater at higher temperatures.

I am glad to acknowledge many helpful discussions with Professor Lennard-Jones on problems of adsorption from which many of the above ideas have emerged.

*Department of Physical Chemistry,
The University, Bristol.*

THE ADSORPTION OF HYDROGEN BY CHARCOAL.

BY F. E. T. KINGMAN.

Received 10th September, 1931.

Some recent work on the adsorption of hydrogen and carbon monoxide by a zinc oxide-chromium oxide catalyst¹ has shown that under certain conditions the adsorption process requires a high heat of activation. Owing to the highly complicated nature of the processes which occur, it was impossible to make any quantitative measurements of this heat of activation. A simpler case was sought for and found in the adsorption of hydrogen on charcoal at 400°-530° C.; the heats of activation of this adsorption process can be determined with a fair degree of accuracy. Preliminary descriptions of this work have already been given,² and further details are given in this paper.

Experimental.

The apparatus was similar to that used in the experiments on the zinc oxide-chromium oxide catalyst¹ with the exception that the adsorption bulb was made of quartz instead of Pyrex.

The charcoal was identical with that previously used in experiments on adsorption of aliphatic alcohols from their aqueous solutions.³ It was a Norit G.R. charcoal, of 60-90 mesh, whose ash content had been reduced to 0.2 per cent. by treatment with hydrochloric and hydrofluoric acids, and which was further cleaned by extremely prolonged treatment with conductivity water to remove any slightly soluble impurity.

The charcoal was activated by heating in an electrical furnace at

¹ Garner and Kingman, *Nature*, **126**, 352, 1930; *Trans. Far. Soc.*, **27**, 322, 1931; Kingman, *Trans. Far. Soc.*, **27**, 654, 1931.

² Kingman, *Nature*, **127**, 742, 1931; *ibid.*, **128**, 272, 1931.

³ Garner and Kingman, *Trans. Far. Soc.*, **25**, 24, 1929.

950° C. under a high vacuum for at least five hours, and treated with hydrogen several times at 400°-500° C. in order to remove any reducible oxygen. At the end of the activation process, the current was cut down to that required to keep the furnace at the temperature at which the adsorption was to take place, and the system left overnight to attain a steady temperature.

In carrying out an experiment, 1.23 c.c. of hydrogen were admitted to the catalyst and readings of the residual pressure taken at regular intervals. The volume which was admitted was much smaller than that required to saturate the charcoal with hydrogen at the temperatures of the experiment and consequently the pressures attained at the end of the experiment were practically zero. Thus it was unnecessary to take the rate of evaporation of hydrogen into account in calculating the velocity of the adsorption from the experimental figures. In between each experiment the adsorbed hydrogen was removed by heating to 950° C. under vacuum.

Results.

It was found that the rate of adsorption of hydrogen at any given temperature was proportional to the pressure and the extent of available surface, that is,

$$-\frac{dp}{dt} = ap(C - x), \quad . \quad . \quad . \quad (1)$$

where x is the volume adsorbed, a and C are constants, $C - x$ being therefore a measure of the available surface. This equation can be reduced to the form,

$$-\frac{dp}{dt} = kp(A + p). \quad . \quad . \quad . \quad (2)$$

From the rate of change of k with temperature, the heat of activation of the adsorption of hydrogen by carbon can be calculated by the use of the equation

$$\frac{d \log k}{dt} = \frac{Q}{RT^2} \quad . \quad . \quad . \quad (3)$$

The first three experiments in the final series gave values of k which were consistently lower than those obtained in the later experiments.

TABLE I.

Expt. No.	Temp. °C.	A .	k .	Heat of Activation.
1	455	0.301	1.51	32,500 calories.
2	530	0.460	12.23	
3	500	0.413	5.46	
5	420	0.248	0.894	
9	472	0.282	4.19	
10	508	0.262	11.31	29,000 calories.
11	470	0.247	4.72	
13	400	0.187	0.568	
14	482	0.320	5.03	
15	429	0.175	1.57	
16	450	0.208	2.96	

This was probably due to a change in the carbon surface through treatment at the high temperatures. The energy of activation calculated from these experiments, however, gave practically identical results with that obtained from the remaining experiments.

It was also observed that a very slight error in the experimental points used to determine A and k had a large effect on the values of A ; but a very much smaller effect on the values of k , which are therefore much more accurate.

Generally speaking, the value of A increases with temperature, but the variations in its value are so large that it is impossible to attach any quantitative physical meaning to this change.

Two typical experiments which show the nature of the agreement with equation (2) are given below.

TABLE II.

t	p (Calc.) (cm.).	p (Obs.) (cm.).	t	p (Calc.) (cm.).	p (Obs.) (cm.).
EXPT. 14. TEMP. = 482° C.					
1.5 (mins.)	0.3752	0.4186	33 (mins.)	0.0267	0.0268
4.5	0.2602	0.2645	39	0.0180	0.0178
9	0.1643	0.1645	45	0.0122	0.0117
15	0.0980	0.0980	51	0.0083	0.0083
21	0.0617	0.0619	57	0.0057	0.0056
27	0.0402	0.0402	63	0.0039	0.0041
EXPT. 5. TEMP. = 420° C.					
0.050 (hrs.)	0.406	0.5119	2.40 (hrs.)	0.0571	0.0568
0.160	0.352	0.389	2.85	0.0433	0.0430
0.300	0.299	0.311	3.60	0.0280	0.0264
0.500	0.243	0.243	4.45	0.0175	0.0171
0.751	0.190	0.190	5.01	0.0130	0.0118
1.05	0.148	0.148	5.50	0.0099	0.0098
1.40	0.113	0.113	6.00	0.0077	0.0076
1.75	0.0875	0.0881	6.53	0.0058	0.0058
2.05	0.0715	0.0733			

The agreement between the calculated and observed values is extremely satisfactory, except for the first few minutes. The rate of reaction in the first few minutes is always greater than that calculated by the equation. This may mean that there are a few very active carbon atoms with which reaction occurs with great rapidity.

The heat of activation has also been calculated from these results by the method used by Taylor and Williamson.⁴ The times taken to reach a definite value of the volume adsorbed, or, as actually in this work, the times taken to reach a definite pressure, with a constant volume admitted, are measured at different temperatures, and the heat of activation calculated from the formula,

$$\log \frac{t_2}{t_1} = \frac{Q}{R} (1/T_2 - 1/T_1),$$

where t_1 and t_2 are the respective times at temperatures of T_1 and T_2 .

The results obtained by this method in experiments 5-16 are given below.

⁴ *J.A.C.S.*, **53**, 2168, 1931.

TABLE III.

Press Range.	Initial p to 3 mm.	3 - 2 mm.	2 - 1 mm.	1 - 0.5 mm.	0.5 - 0.2 mm.
Heat of activation (cals.)	27,500	30,000	32,000	32,500	31,000

The value of the heat of activation is thus the same by both methods of calculation, that, is, 30,000 calories. It will be noted that the first value, corresponding to the fall in pressure for the first few minutes is lower than that reached subsequently. This would be expected in view of the results in Table II.

Discussion.

The theory of activation energy of adsorption processes put forward by Taylor⁴ has been criticised by Steacie⁵ on the ground that in most of the cases where according to Taylor it is necessary to assume a heat of activation to occur, the phenomena can be adequately explained by the occurrence of solution of the adsorbed gas in the interior of the catalyst.

It has been shown in this research, however, that in the case of the adsorption of hydrogen on carbon, where the rate of adsorption is measurable, the rate of adsorption is proceeding at a rate governed by the pressure and the extent of available surface, and that the rate can be accurately expressed by an equation containing these two factors. This would not be the case if the rate of diffusion were the dominant rate.

The heat of activation is practically constant over the range of adsorption (0 to 0.3 c.c./gm. charcoal) used in this experiment, whereas Taylor found that the heat increased with increase in the volume adsorbed in the case of manganous oxide catalysts. This difference may be due to the fact that in this research, the amounts of hydrogen which were adsorbed on carbon were small compared with the total amount of hydrogen which could be taken up. Thus, the fact that the critical increment is independent of the fraction of the area covered may only hold for the more active and readily accessible portion of the carbon surface.

It is difficult to decide whether or no the hydrogen enters into chemical combination with the carbon, to form CH-groups on the surface.

Summary.

The adsorption of hydrogen by charcoal has been studied at 400°-530° C., and the rate of adsorption has been shown to obey a simple law. The critical increment of the process has been determined as 30,000 calories.

The author wishes to express his thanks to Professor W. E. Garner for his constant interest and advice during the course of this investigation.

*Department of Physical Chemistry,
The University, Bristol.*

⁵ *J. phys. Chem.*, **35**, 2168, 1931.

THE SORPTION OF HYDROGEN BY PLATINISED CHARCOAL.

BY R. BURSTEIN AND A. FRUMKIN.

Received 29th December, 1931

It was shown in previous papers from this laboratory¹ that the introduction of small quantities of platinum into ash-free activated charcoal strongly influences its behaviour in the presence of aqueous solutions of electrolytes. While unplatnised charcoal which has ad-

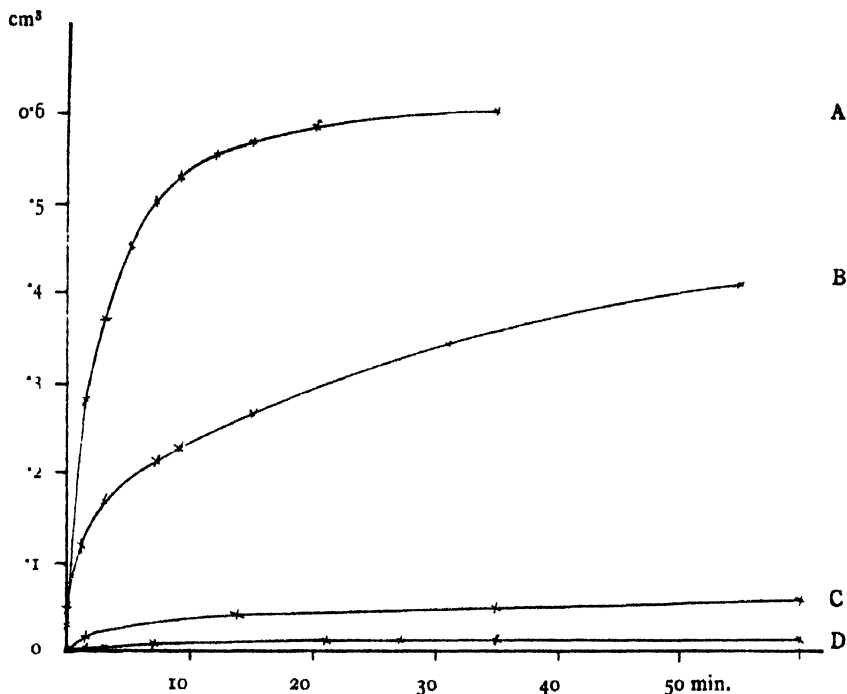


FIG. 1.—Adsorption of hydrogen by charcoal at different temperatures.
A, 500°; B, 310°; C, 200°; D, 25°.

sorbed oxygen keeps its oxygen charge in a hydrogen atmosphere, the oxygen layer is removed by hydrogen from charcoal which has been promoted by platinum and the positive oxygen charcoal is changed into a negative hydrogen charcoal. In the presence of insufficient quantities of platinum transitional states are observed, but adsorption measurements show us that a transitional state of this kind is not due to a simultaneous existence of positive and negative spots on the charcoal surface, the charge being always the same at all points of the charcoal surface for a given content of platinum and gradually changing from positive

¹ B. Bruns and A. Frumkin, *Z. physik. Chem.*, **141A**, 141, 1929; A. Frumkin, S. Lewina and O. Zarubina, *ibid.*, **155**, 71, 1931; A. Frumkin, *Koll. Z.*, **51**, 123, 1930.

to negative as the platinum amount is increased. It appeared therefore worth while to investigate whether the process of interaction between a bare, oxygen-free charcoal surface and hydrogen is catalysed by platinum and whether, in this case too, the properties of the whole surface of charcoal are changed when a small part of it is covered with platinum. The experiments performed up to now are insufficient to give an answer to the second question, but they show conclusively that platinum catalyses the hydrogen sorption by charcoal.

Experimental.

The charcoal used was activated ash-free sugar charcoal; the mode of preparation and of introducing the platinum was the same as described by Bruns and Frumkin.¹ The charcoal was outgassed for twenty-seven

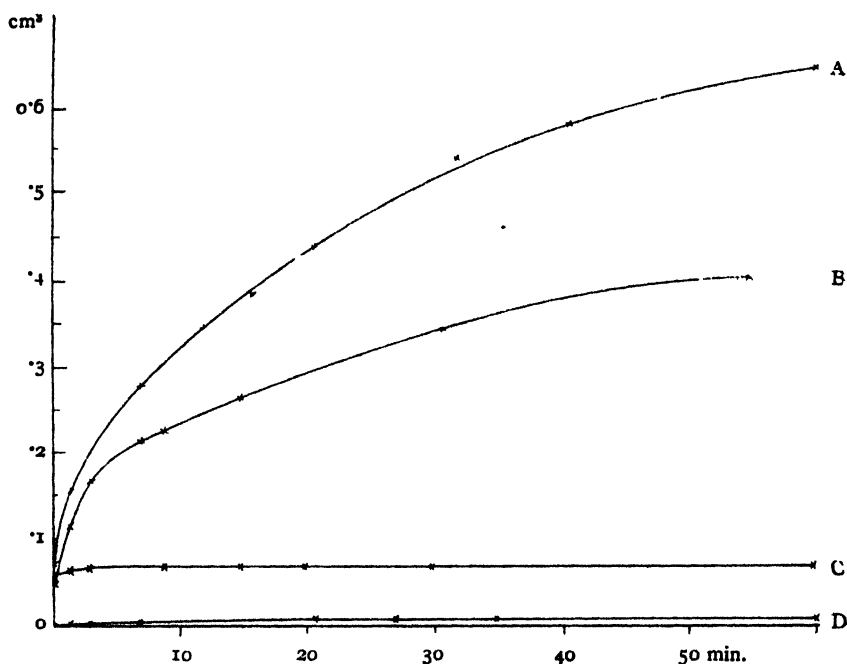


FIG. 2.—Influence of platinum on the adsorption of hydrogen by charcoal.

Curve A. 310°, 0.2 % Pt.

Curve B. 310°, 0 % Pt.

„ C. 25°, 0.2 % Pt.

„ D. 25°, 0 % Pt.

hours at 900° C. under vacuum before being brought into contact with the hydrogen.

Fig. 1 shows the kinetics of the hydrogen adsorption at different temperatures in c.c. of hydrogen (at 760 mm. and 0° C.) per 10 gr. of charcoal. The initial pressure was 1.5 mm., the volume of the apparatus about 250 c.c. and the actual amount of the charcoal used in the experiments 5 gr.

Fig. 2 shows the influence of the platinum (0.2 per cent. Pt). The initial pressure was 0.23 mm. in the experiments at 25° C. and 1.5 mm. in those at 310° C.

Discussion.

The adsorption of hydrogen on charcoal is an example of "activated" adsorption, as has already been shown by Kingman.² This is confirmed by our measurements on activated sugar charcoal, the amount adsorbed rising strongly with increasing temperature. Schuster³ observed a similar increase of the low pressure hydrogen adsorption with rising temperature but the kinetical behaviour of Schuster's charcoal was different, as the equilibrium pressure was practically reached in one minute. This was a technical charcoal, which contained iron and traces of copper. It is not quite certain whether hydrogen adsorption by charcoal is completely reversible, since on outgassing the charcoal which has adsorbed hydrogen the formation of small amounts of a dark deposit on the walls of the reaction vessel is always observed; this is probably due to the decomposition of some hydrocarbons. As shown by the curves of Fig. 2, platinum enhances the activity of charcoal towards hydrogen, although the effect is rather smaller as we have expected on the basis of experiments mentioned at the beginning of this note. We hope to continue this work on different lines and to compare the influence of the platinum on the hydrogen adsorption with its effect on the activity of charcoal in various hydrogenation processes.

*Karpow Chemical Institute,
Moscow.*

² *Nature*, **127**, 742, 1931; **128**, 272, 1931.

³ *Z. physik. Chem.*, **14B**, 253, 1931.

THE KINETICS OF ADSORPTION PROCESSES. II. THE OCCLUSION OF HYDROGEN BY PALLADIUM. PART I. DISCUSSION.

By A. R. UBBELOHDE, B.A., B.Sc.

Received 7th December, 1931.

Since the original experiments described by Graham¹ a large number of publications have appeared on this subject. Many of the earlier experiments have since been repeated with more elaborate technique; a summary of the literature up to the year 1900 was given by Bose²; for references to later work *cf.* Lambert and Gates,³ Tammann,⁴ and Coehn and Specht.⁵ Various contributions to the subject were also made at a meeting of the Faraday Society in 1919.^{2b} The object of this communication is to co-ordinate various theories that have been put forward to explain the phenomena.

Metallic palladium will occlude large volumes of hydrogen under suitable conditions, either on being exposed to hydrogen gas, or when it is used as a cathode in electrolysis. Palladium occludes hydrogen during electrolysis without difficulty, but sorption from the gas phase depends to a marked extent upon the previous history of the metal. The maximum amount occluded in either case is about the same, so that this characteristic difference in behaviour must be due to the fact

that palladium absorbs hydrogen atoms, as discharged at a cathode, without any difficulty, whereas hydrogen molecules do not enter so easily.

The explanation adopted here is that hydrogen may be adsorbed on the surface of palladium either as atoms or molecules, but that it penetrates into the metal lattice only in the form of atoms, which may be ionised. Before hydrogen can be absorbed by palladium, the reaction $H_2 \rightarrow 2H$ must take place on the metal surface. For this reaction a catalyst is necessary, and different samples of palladium show marked differences in the velocity with which they absorb hydrogen, according as the active points on the metal surface are more or less poisoned. On desorption different samples of palladium do not show such large differences. Using the approximate formula for the dissociation of a diatomic gas,

$$\log K_p = -q/4.57T + 1.75 \log T, \text{ the value of } \log K_p \text{ at } 100^\circ \text{C,}$$

taking q to be 105,000 cal., is -57.1 . The relative velocities of the reactions $H_2 \rightarrow 2H$ and $2H \rightarrow H_2$ in the gas phase are thus very different. If the same velocities held in the adsorbed layer, and if desorption equilibrium took one hour, adsorption equilibrium under the same conditions would take about 10^{50} years. Thus in the desorption isothermals obtained by Lambert and Gates³ equilibrium is reached fairly rapidly, whereas in the adsorption isothermals more or less hysteresis is observed.

Evidence for the Atomic Condition of the Dissolved Hydrogen.

—According to Sieverts⁶ the occlusion L of hydrogen by palladium is represented at low pressures and over a large range of temperatures by an equation of the form

$$L = k_1\sqrt{p} + k_2p \text{ where } k_2 \text{ is small compared with } k_1.$$

The fact that the solubility is practically proportional to the square root of the pressure is usually explained by assuming that the hydrogen dissolves as atoms. The (very small) concentration of H atoms in the gas phase is proportional to the square root of the pressure, and if Henry's law is obeyed the concentration in the solid phase will also be proportional to the square root of the pressure.

Two objections have been raised against this interpretation. According to Tammann,⁴ Henry's law may only be applied to reversible systems, whereas in the case of hydrogen and palladium marked hysteresis is observed. Actually in the region of pressures where the relation holds, little or no hysteresis has been observed (Lambert and Gates,³), but even if the relation held only for the removal isothermal, where equilibrium is most rapid, the thermodynamical interpretation would be valid. Ward⁷ has pointed out in his study of the adsorption of hydrogen on copper that a square root relationship will be obtained if the molecules evaporate in pairs, so that no dissociation into atoms need be assumed. Unless the lateral adhesion between pairs of hydrogen molecules is large compared with their adhesion to the surface, it is difficult to see why molecules should evaporate in pairs. Considerable further evidence for the existence of atoms in solution makes this alternative explanation unnecessary in the case of palladium.

Hydrogen atoms in palladium explain the profound influence of the occlusion of hydrogen on the electronic properties of the metal, such as the electrical resistance (recent papers are quoted in⁸), the magnetic

susceptibility,⁸ the colour (a darkening takes place on occlusion),³ the photo-electric sensitivity,⁹ and the thermo-e.m.f. against alloys of palladium with silver and gold.¹⁰ The ease of diffusion of hydrogen through palladium foil, used as cathode, has recently been demonstrated still more clearly by Coehn and Specht.⁵ These authors showed that the hydrogen in palladium will move along a palladium wire if a potential gradient is set up; the effect was obtained even with the smallest potential gradients that could be applied, and the results were interpreted by assuming that the hydrogen atoms in the metal are dissociated into protons and electrons. Very little if any work is required to move the protons from point to point in the lattice. The particular experiments quoted might be explained by assuming the presence of H_2^+ in the palladium, but only the assumption of the presence of atoms explains all the results without special hypothesis.

Energy Relationships of the System.—The heat of occlusion of hydrogen by palladium has been determined directly by Mond, Ramsay and Shields,²⁶ and has been calculated from the position of the isothermals at different temperatures (Partington,²² Gillespie and Hall¹⁶). Both methods show that about 9,000 cal. are evolved when occlusion takes place; the heat of occlusion at low pressures¹⁶ is apparently definitely smaller. If it is assumed that in Sieverts' equation⁶ $L = k_1\sqrt{p} + k_2p$ the term in \sqrt{p} is due to solution, the term in p to surface adsorption (see later), values of the heats of solution and adsorption can also be calculated from the values of k_1 and k_2 at different temperatures. The heat of adsorption varies irregularly from 700 to 8000 cal., and the heat of solution decreases regularly from about 1500 cal. at *circa* 500° to about 800 cal. at 700° C. These values cannot be compared with those of the previously cited authors, since they refer to higher temperatures. No experiments have been discovered in the literature referring to the specific heat of palladium containing occluded hydrogen; * the difference in specific heats between $4Pd + H_2$ and $2Pd_2H$ may be estimated at *circa* 8 cal., if the hydrogen is dissociated into atoms and takes part in the thermal oscillations of the metal lattice. This would make the large temperature coefficient of the heat of solution, as calculated from Sieverts' data, fairly easy to understand. Another reason for the falling off in the heat of occlusion at high temperatures may be that an increasing dissociation of H atoms into protons and electrons takes place. Determinations of the specific heat would clearly be of interest.

An objection raised by Tammann⁴ against the presence of H atoms in palladium may be discussed here. He pointed out that the ease with which the "compound" Pd_2H is dissociated could not be reconciled with the heat of the reaction $2Pd + H = Pd_2H + 50,000$ cal. According to the explanation already outlined, the "compound" does not dissociate in this manner. The hydrogen is spread throughout the metal lattice as atoms, but only leaves the metal as molecules, after the reaction $2H = H_2$ at active points in the surface. The dissociation of the "compound" should therefore be written $2Pd_2H = 4Pd + H_2 - 9000$ cal.; this heat is of the order required to give the observed dissociation pressures (a closer calculation using the heat theorem is not possible for lack of data).

The heat of union of H atoms with Pd must, however, be of the order

* Except a single result given by Beketoff for atomic heat of hydrogen in Pd, 5.88 at room temperature (*Ber.*, 12, 686, 1879).

of 50,000 cal. Taking the boiling-point of Pd to be 2810° K, the latent heat from Trouton's rule (*cf.* ³⁰ for its applicability) will be 62,000 cal. Since the interpenetration of Pd and H atoms is probably at least as great as that of two Pd atoms, the heat of 50,000 cal. which must be ascribed to the reaction $\text{Pd} + \text{H (gas)} = \text{PdH (solid)}$ is not at all improbable.

If the H atoms are dissociated into protons and electrons, the additional energy required, calculated from the ionisation of gaseous H atoms, would be about 300,000 cal. (*cf.* ⁵). This energy must be supplied by the affinity of the metal for electrons. K. Bennewitz and P. Gunther ²⁹ point out that the work of ionisation of a hydrogen atom in a medium of infinite dielectric capacity, such as a metal, will be zero. At present not enough facts are known to decide whether all the H atoms are dissociated, or whether an equilibrium exists between H atoms, electrons and protons.

Evidence from the Physical Condition of the Metal.—The evidence for the existence of more than one solid phase is still debatable. According to Hoitsema ¹¹ and Gillespie and Hall ¹⁶ the existence of a region or "flat part" on the removal isothermals where the pressure is constant is to be explained by the assumption of two phases, since only two components are involved in the system. It is doubtful, however, whether the pressure does not fall slowly over the flat part (reference ³ and the experiments to be described later), particularly at higher temperatures: ¹¹ unless the pressure remains absolutely constant the phase rule argument does not apply. From a study of the thermal effects of heating and cooling Pd in H_2 Andrews and Holt (¹² *cf.* ²²) inferred the existence of two forms of the metal, but it seems more plausible to suppose that "amorphous" and "crystalline" Pd differ in their effectiveness as catalysts for the reaction $\text{H}_2 \rightarrow 2\text{H}$ without forming distinct phases once the occlusion has taken place. Deformation of the lattice would influence the absorptibility.

The evidence from X-ray studies on Pd/H is again somewhat contradictory. Different authors agree that the lattice merely expands as hydrogen enters, but Yamada ¹³ obtained a continuous expansion, whereas Linde and Borelius ¹⁴ found a range of low or of high values of the lattice constant, the intermediate values being missing. The intensity maxima of the "hydride" are also said to be different. If intermediate stages are really missing in the expansion of the lattice, this would be a strong argument for the existence of two solid solutions, but the short time given for equilibrium, and the lack of precautions against poisoning (see later), may have led to the palladium used by these authors being sometimes in an active and sometimes in a passive state, which would mean that in some cases a large amount of hydrogen is absorbed, in some cases very little. The absence of intermediate values may thus be fortuitous. (See however ³².)

Other evidence for the structure of the solid phase is based on the continuous or discontinuous increase of certain magnitudes, such as volume, ²³ electrical resistance, and magnetic susceptibility (*vide supra*), as the amount of occluded hydrogen increases. In general no great discontinuities are observed up to the point Pd_2H .

Although it is improbable that a fresh phase is formed when hydrogen is occluded by palladium, there is considerable evidence that when once hydrogen has entered the solid phase up to the proportions given very approximately by Pd_2H any further hydrogen that can be made to enter

the palladium is much more loosely held (for breaks at Pd_2H see ^{3, 5, 8}, for the effect of replacing Pd by other atoms see ¹⁵, but also ¹⁰). The condition of the solid phase is best described by assuming with Tammann ⁴ that hydrogen enters the lattice, and that all the spaces are occupied with hydrogen atoms when the ratio H/Pd reaches the value 0.5.

A kinetic explanation for the flat part may perhaps be developed as follows: There is considerable evidence that Pd adsorbs hydrogen on its surface, like other transitional elements (*cf.* the larger adsorption of colloidal Pd ²⁴, and ²⁷). The adsorption is not very large,⁶ and may be assumed proportional to the pressure (see later). If the number of active points on the surface is z , the fraction occupied will be bpx , where b is constant at constant temperature. The rate of entry into the lattice will be $bdpx$, where d is a constant at constant temperature (d involves the energy necessary for the activation of the reaction $\text{H}_2 \rightarrow 2\text{H}$). The rate of loss of hydrogen from the lattice near the surface depends *inter alia* upon the rate of diffusion of the atoms, but if the rate of loss is small compared with the rate at which fresh atoms can travel to the surface, the rate of loss will be practically independent of the concentration of hydrogen in the solid phase; we may write it fz , where f is nearly constant at constant temperature. At equilibrium, $bdpx = fz$, *i.e.*, $p = \text{constant}$. Thus a flat part will be obtained as long as the velocity of diffusion of H atoms or protons is more than sufficient to supply the rate of loss. As the concentration in the solid phase diminishes, a region is reached where this no longer holds, and the rate of loss depends upon the concentration in the solid phase. The third branch of the isothermal, beyond the point Pd_2H , may be due to surface adsorption only, or to the additional hydrogen in the lattice leaving it by another mechanism. Experimental evidence for this explanation will be given in Part II.

Velocity of Occlusion: Qualitative Observations.

The velocity of occlusion will be governed by three main factors: (a) the velocity of adsorption (or desorption), (b) the rate at which the reaction $\text{H}_2 \rightarrow 2\text{H}$ takes place, (c) the rate of diffusion into the interior. Both (a) and (b) may require initial activation of the molecule, and will thus depend on the state of the metal surface (number of active points, poisons, etc.), whereas (c) will not be a factor of great importance except at very low temperatures, where the velocity of diffusion is slow,⁵ and comparable with the rate at which the molecules cross the phase boundary.

Numerous qualitative observations on the rate of occlusion, and on active and inactive palladium have been recorded. Two processes are helpful in activation. (a) Repeated oxidation and reduction apparently increase the number of active points in the surface (*cf.* amorphous Pd ²²) whereas heating to high temperatures is followed by sintering and deactivation,¹⁷ (see below). (b) The removal of poisons greatly accelerates occlusion. The number of poisons whose influence has been definitely tested is not very great. The effect of H_2S has been noted by Valentiner,²⁸ but the most usual poison is oxygen. Sieverts noted that the alloy 60 per cent. Pd, 40 per cent. Ag (which shows a maximum solubility for H_2) could not be reactivated once air had been let in, even though the alloy was heated to 820°C . in hydrogen.¹⁰ Firth ²⁷ described an experiment which showed the connection between inactivity and a protective film of PdO. Tammann and Schneider ¹⁷ showed that after palladium charged with hydrogen had been exposed to air, the velocity

of occlusion decreased, and it was very difficult to reactivate it. The most probable explanation of this poisoning is that oxygen is strongly adsorbed on the active points in the surface, thus rendering them unavailable for catalysis of the reaction $H_2 \rightarrow 2H$. Experimental evidence of this effect is given, see Part II. The effect of mercury vapour as a gradual poison for Pd³¹ has not been definitely confirmed, but it is certain that unless specially pure hydrogen is used the palladium gradually loses its activity.²⁵

Criteria as to the activity of the palladium are very important in discussing the interpretation of adsorption and desorption isothermals.^{3, 16, 25} When hydrogen (which generally contains a minute amount of oxygen as impurity, even if passed over palladinised asbestos), is added to palladium, occlusion takes place, but the surface is gradually poisoned. If more hydrogen is added at a time, the poisoning (which depends on the total number of oxygen atoms) will be more rapid, and less will enter. If the temperature of the system be suddenly lowered, a certain amount of hydrogen will leave the palladium, since the gas phase will be cooled more rapidly than the metal (*cf.* 16). The peculiarity of the "equilibrium" under discussion is that it is much more easy for hydrogen to leave the palladium than to re-enter it. If the system be warmed up to the initial temperature once more, there will still be an excess of hydrogen in the gas phase, and the pressure will in general be higher than before (see Lambert and Gates).³

The heat treatment, with which Gillespie and Hall¹⁶ could hasten desorption but not absorption equilibrium, no doubt reactivates the palladium, which is fairly soon poisoned again. These theoretical descriptions of the behaviour of the system are given to show that the peculiar phenomena shown by the system palladium/hydrogen³ can be explained in terms of the catalytic efficiency of the surface for the dissociation of hydrogen.

As long as the pressure never rises *above* the equilibrium value, the pressures obtained on the removal isothermal will be the same as if equilibrium were very fast indeed. On the addition isothermals true equilibrium is not obtained; the curves showing the relation between pressure and mass added are unexpectedly smooth, but this may be due to the fact that addition took place in regular increments.

Experiments on the diffusion of gaseous hydrogen through palladium^{25, 31} are subject to the same irregular variations as experiments on the velocity of occlusion, and these variations are almost certainly due to chance poisoning.

Velocity of Occlusion.

Consider a sorbent bombarded by molecules of the sorbate. If n_0 molecules strike unit surface of the sorbent per second, and the fraction a pass into the sorbed condition, the velocity of sorption may be defined as an_0 . The fraction a will not in general be equal to unity, either because a number of the bombarding molecules strike "elementary spaces" that are already occupied or inactive, as in the Langmuir theory of adsorption¹⁹ or because only molecules with sufficient energy of activation can pass into the adsorbed condition,²⁰ or because certain other conditions such as appropriate orientation must be fulfilled. In general, $a = fke^{-E/RT}$, where f is the fraction of the total surface available, E the activation required for sorption, k a constant determined by other conditions necessary for sorption.

Although the interpretation of a is not quite so simple as that of an analogous quantity in gas reactions, it is obviously of interest to determine a experimentally. Two types of experiment are available for the calculation of a :—

(1) **Direct Determination of the Velocity of Desorption or Sorption.**—In the experiments of Tammann and Schneider (¹⁷ cf. also the earlier work in ¹⁸ and ²⁵) a piece of Pd charged with hydrogen is suddenly exposed to vacuo, and the rate of rise of pressure determined, or else hydrogen is suddenly brought into contact with previously evacuated Pd, and the rate of fall of pressure measured. If the volume of the vessel is known, the number of moles n changing state per second can be calculated from the pressure and temperature. The value of n at the beginning of the experiment will be undisturbed by gas already adsorbed or desorbed, and may be found by extrapolating back to zero time.

In the case of adsorption experiments, if s is the surface of the sorbent, the total number of moles psn_0 striking the surface per second is $pus_0 = sp\sqrt{(M/2\pi RT)} = 0.0583 sp\sqrt{(M/T)}$, where p is in mm. Hg. Here a is simply $a = n/(psn_0)$.

The experiments were not carried out with the purpose of determining a , and the following calculation is rough for want of appropriate data :—

Temperature of vessel = 100° C. approx.

Volume not stated, but if it is assumed the total drop in pressure is proportional to the total mass adsorbed, and taking the average rate of fall of pressure over the first few minutes, n may be estimated as 1.3×10^{-8} moles per second, $n_0 = 3.15$ moles/sec., and $s = 4$ cm.² approx., so that $a = 1.0 \times 10^{-9}$

According to the authors, the velocity of sorption during the first few minutes is practically constant. This agrees with the view that the rate of the reaction $H_2 \rightarrow 2H$ is the deciding factor in the rate of absorption; in the later stages the absorption slows down either because of a gradual poisoning of the surface, or because the diffusion into the interior is compensated by re-evaporation. If the only factor influencing a is the activation required for occlusion $fk = 1$, and the value of E , the activation energy, works out to be 15,400 cal. (This value is relatively insensitive to changes in a , e.g., if a were 2.7×10^{-9} E would be 15,100 cal.). Any factor influencing a independent of activation would make the above value of E too large.

A second method of estimating the activation necessary for occlusion involves a comparison of the initial velocities of adsorption at different temperatures. After correcting for the change in n_0 with temperature, the initial velocities are proportional to the values of a . Tammann and Schneider heated their palladium foil to high temperatures and then determined the velocities of adsorption at 373° K, 423° K, and 473° K. The following table is calculated from their results :—

Previous Heat Treatment.	E Calc. from 373° to 423° K.	E calc. from $423/473$.
500° C.	10.900	—
700° C.	12.400	—
800° C.	15.800	7,800
1000° C.	17.300	5,900

In view of the rough calculation, the values of E as calculated in the middle column are in satisfactory agreement with that obtained by the first method, though probably the higher value obtained by the first method is due to the fact that $fk \neq 1$ in the above equation (this influence cancels out in the second method). More severe heat treatment increases the value of E . If all the catalytic points were the same, but merely diminished in number as the heat treatment was more severe, E would remain constant. Clearly sintering removes the more active points or (*cf.* Tammann) exposes the less active crystal planes. (The values of E for the range 423° to 473° K are probably too low, as the velocity of adsorption in the individual experiments does not remain constant for long, and the initial velocity has probably been underestimated.)

(2) **Determination of the Value of α From the "Dynamic Isothermals."** In a previous publication²¹ a method has been described for obtaining adsorption isothermals at different rates of removal of the sorbate. The essence of the method is to exhaust the adsorption system continuously through a graduated capillary. If P is the pressure at any moment in the system, the rate of loss of sorbate is kP^2 , where k is a constant depending on the resistance of the capillary and the temperature of the gas. The isothermal obtained by plotting the mass removed against the pressure lags behind the equilibrium isothermal by an amount depending upon α .

Suppose that when a given mass of gas is present in the system, the equilibrium pressure is p_0 , the actual pressure p . The lag L is defined as $L = p_0 - p$. Using the same notation as before, the number of moles evaporating/sec. is p_0san_0 , since this would be the number condensing at equilibrium. The number of molecules actually condensing is, however, $psan_0$ (a may be assumed to be the same as at equilibrium unless the lag is large). Thus the nett rate of evaporation into the free space above the sorbent is $Lsan_0$. The nett rate of loss of gas from the free space is kP^2 . If N is the number of moles in the free space of volume V and temperature T ,

$$dN/dt = Lsan_0 - kP^2 = (V/RT)dp/dt,$$

or

$$(V/RT)dp/kp^2dt = (Lsan_0/kp^2 - 1) \quad (1)$$

In this equation the different quantities are determined experimentally as follows: V/RT from the volume of the reaction system. If the system be initially in equilibrium, $L = 0$ when $t = 0$, so that V/RT may also be found by extrapolating the value of dp/dt back to zero time.

k is known from the calibration of the capillary, p by direct measurement, and s also, if the sorbent has a measurable surface, and n_0 from the kinetic theory of gases.

L is best determined by plotting the complete equilibrium isothermal and a number of dynamic isothermals with different k 's on the same scale. Such a plot alone, without further calculation, provides information about the particular type of sorption shown by the system under examination (see below, and *cf.* 21).

In general, the direct determination of the velocity of adsorption would probably give more accurate individual values of α , on account of the simple formula used in calculation. The method of "dynamic isothermals" enables a survey of the adsorption over a wide range of pressures to be made in a remarkably short time.

The experiments on this basis which are described in Part II. have been used to arrive at the value of a and can be interpreted according to the hypothesis favoured in the above discussion. The effect of poisoning of the surface is shown to be very marked.

Summary.

After discussing the evidence that hydrogen enters the palladium lattice as atoms, equations are given for the velocity of this process under various experimental conditions. The different factors influencing the velocity of occlusion are also discussed, and a simple explanation is given for the fact that equilibrium is much more rapid on desorption than on adsorption.

REFERENCES.

References are given only to papers quoted in the discussion, but the list may be supplemented on consulting the authors cited in the introductory paragraph.

- ¹ T. Graham, *Proc. Roy. Soc.*, **16**, 422, 1867.
- ² E. Bose, *Z. physik. Chem.*, **34**, 701, 1900.
- ³ B. Lambert and S. F. Gates, *Proc. Roy. Soc.*, **108A**, 456, 1925.
- ⁴ G. Tammann, *Z. anorg. Chem.*, **188**, 396, 1930.
- ⁵ A. Coehn and W. Specht, *Z. Physik*, **62**, 1, 1930.
- ⁶ A. Sieverts, *Z. physik. Chem.*, **88**, 103 and 451, 1914.
- ⁷ A. Ward, *Proc. Roy. Soc.*, **133A**, 531, 1931.
- ⁸ J. Aharoni and F. Simon, *Z. physik. Chem.*, **4B**, 175, 1929; Oxley, *Proc. Roy. Soc.*, **101A**, 264, 1922.
- ⁹ F. Kruger and A. Ehner, *Z. Physik*, **14**, 1, 1923.
- ¹⁰ A. Sieverts, *Z. anorg. Chem.*, **92**, 329, 1915.
- ¹¹ Hoitsema, *Z. physik. Chem.*, **17**, 1, 1895.
- ¹² Andrews and Holt, *Proc. Roy. Soc.*, **89**, 170, 1914.
- ¹³ M. Yamada, *Phil. Mag.*, **45**, 241, 1923.
- ¹⁴ J. Linde and G. Borelius, *Ann. Physik*, **84**, 747, 1927.
- ¹⁵ L. Nowack, *Z. anorg. Chem.*, **113**, 14, 1920.
- ¹⁶ Gillespie and Hall, *J.A.C.S.*, **1207**, 1926.
- ¹⁷ G. Tammann and J. Schneider, *Z. anorg. Chem.*, **172**, 43, 1927.
- ¹⁸ A. Holt, *Proc. Roy. Soc.*, **90A**, 226, 1914.
- ¹⁹ I. Langmuir, *J.A.C.S.*, **40**, 1361, 1918.
- ²⁰ H. S. Taylor, *J.A.C.S.*, **53**, 578, 1931.
- ²¹ Ubbelohde and Egerton, *Proc. Roy. Soc.*, **134**, 512, 1931.
- ²² *Occlusion of Gases by Metals*, *Trans. Faraday Soc.*, **14**, 173, 1919.
- ²³ M. Thoma, *Z. physik. Chem.*, **69**, 3, 1889.
- ²⁴ C. Paal and C. Amberger, *Ber. deut. Chem. Ges.*, **40**, 2209, 1905.
- ²⁵ Holt, Edgar and Firth, *Z. physik. Chem.*, **82**, 513, 1913; Holt, *Proc. Roy. Soc.*, **91**, 148, 1915.
- ²⁶ Mond, Ramsay and Shields, *Proc. Roy. Soc.*, **62**, 290, 1898.
- ²⁷ J. Firth, *J.C.S.*, **117**, 171, 1920; *id.*, *J.C.S.*, **119**, 1120, 1921.
- ²⁸ Valentiner, *Ber. deut. Physik. Ges.*, **3**, 1003, 1911; E. B. Maxted, *J.C.S.*, **115**, 1050, 1919.
- ²⁹ K. Bennowitz and P. Gunther, *Z. physik. Chem.*, **111**, 257, 1924.
- ³⁰ P. Harteck, *Z. physik. Chem.*, **134**, 17, 1928.
- ³¹ W. Ramsay, *Phil. Mag.*, **38**, (v), 206, 1894; C. Paal and H. Steyn, *Ber. d. Chem. Ges.*, **51**, 711, 1918.
- ³² L. W. McKechan, *Physical Rev.*, **21**, 334, 1923.
- ³³ Pease and Taylor, *J.A.C.S.*, **44**, 1632, 1922; Larson and Smith, *J.A.C.S.*, **47**, 346, 1926.

THE KINETICS OF ADSORPTION PROCESSES. THE OCCLUSION OF HYDROGEN BY PALLADIUM. PART II. DYNAMIC ISOTHERMALS.*

BY A. R. UBBELOHDE, B.A., B.Sc., AND A. EGERTON, F.R.S.

Received 7th December, 1931.

The method employed for the determination of the isothermals of the system Palladium/hydrogen was similar to that for the system Charcoal/hydrogen already described,²¹ and the experimental arrangements were very much the same, and need no detailed description. The reaction vessel containing granular palladium was kindly lent by Dr. Lambert, and was the same as that used in the researches described in ³. The uncertainty in evaluating the surface of granular palladium is somewhat greater than when foil is used, but it was thought desirable to use a sample of the metal whose previous history was well known. Examination of the sample showed that it consisted of coherent granules of an average diameter of 0.6 mm. (± 0.1 mm.). The surface of the granules was not smooth, but was made up of little dimples and points of an average diameter of 0.005 mm. These would more than double the surface. The weight of palladium used was 4.75 grms. Assuming the density to be 11.4 grms./c.c. and the granules to be compact spherical particles with dimpled surfaces, the available surface of the sample works out to be at least 83.2 cm.², and probably many times greater.

The reaction system could be connected with a high velocity vacuum pump by means of a calibrated capillary, and the pressure was read at intervals on a mercury manometer, as in the experiments already described.²¹

The temperature of the reaction vessel was controlled by means of a vapour bath, and the vessel containing the palladium was protected from droplets of cold liquid, and from radiation losses by a metal sheath. The normal boiling-points of the purified substances used were: benzophenone 305.9° C., naphthalene 217.97° C., bromobenzene 156° C., and water 100° C.

Investigation was first made of the removal isothermals, since according to Lambert and Gates,³ these alone are reproducible. In order to study the dynamic addition isothermals certain changes in the apparatus are necessary. Only the removal isothermals are discussed here.

Each dynamic isothermal is obtained as follows: after a specified pre-treatment (see below) pure hydrogen from a reservoir is let into the reaction vessel up to a pressure of about 40 cms. The system is then left to come to equilibrium for an hour or more (it is not essential that equilibrium should be reached), and the tap to the capillary is then opened. The level of the manometer columns is read every minute, and from these readings the pressure in the vessel at any time is computed. The mass of gas escaped is $\int kp^2 dt$. Suitable approximations to this integral have been described in ²¹. From the pressure and the mass escaped the "dynamic isothermal" can be plotted.

* For reference to literature see Part I., on previous page.

Summary of the Experiments.

The dynamic isothermals were first determined at each of the temperatures mentioned, using two capillaries which let through 2.0 and 8.0×10^{-7} moles of hydrogen per minute under a difference of pressure of 1 cm. Hg. Secondly, the effect of specified pre-treatment on the form of the adsorption isothermal at 100°C. was tested.

Experiments above 150°C. —The dynamic isothermals at each of the three temperatures 306° , 218° , 156°C. , are practically straight lines, with *no* evidence of a flat part under the conditions of these experiments. The slope dp/dm gradually gets bigger as the pressure drops, more so below 9 cm. Hg. With the faster rate of removal the slope is less, particularly in the early stages. This indicates that the drop in

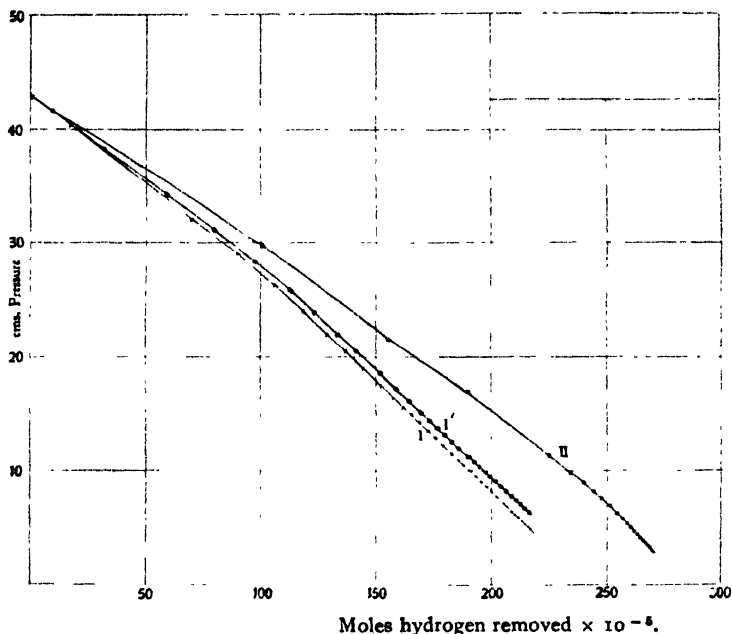


FIG. 1.—Dynamic Isotherms at 306°C.

Curve I Capillary I. Curve II Capillary II.
Curve I' Capillary I.

temperature due to the evaporation of hydrogen is quite considerable at rates of removal employed. Isotherms determined for the system at 306°C. at different times were not very reproducible, probably on account of uncontrolled poisoning (see Fig. 1). This lack of reproducibility means that the system is not suitable for calculation of a for different parts of the same isothermal. The equation,

$$(V/RT)dp/kp^2dt = (Lsan_0)/kp^2 - 1,$$

may however be used to calculate a single value of a for each experiment, just as in the direct method of determining adsorption velocity. L is put equal to the total drop in pressure from the beginning of the experiment; actually $L = p_0 - p$ must be smaller than this, but the table given below shows that no serious error is introduced by this assumption, since the values of a do not change much with pressure.

TABLE I. (579° K.).

Pressure.	Pressure Drop.	$a \cdot 10^6$
40.647 cms.	(start)	0.14
35.991 "	4.656	.11
32.076 "	8.571	.09
28.932 "	11.715	.07
26.278 "	14.369	.06
24.062 "	16.585	.06

The values of a at zero time are obtained by extrapolation, and are given for the different experiments in Table II. (The initial pressure in each experiment is about the same.)

TABLE II.

Temperature.	$a \times 10^6$.	E_1 , cal.	E_2 , cal.
579° K.	0.14	20.700	—
579	.08	21.600	— (probably a minute leak of air)
579	.15	20.700	—
579	.15	20.700	—
491	.11	17.900	2,800
430	.03	16.800	8,900
373	.33	12.700	— (abnormally active Pd.)

The third column gives the value of E_1 , the activation energy, if a were due entirely to the necessity for activation. The fourth column gives the value of the activation energy from the ratios of a at different temperatures. It will be seen that other factors besides activation energy have a very decided influence upon a . The most important of these is almost certainly the extent of the active surface of palladium, or the number of active points per cm^2 . In calculating a , the total surface of 83.2 cm^2 (which is probably underestimated) was assumed to be active. The difference between the true energy of activation and the value of E at any temperature must be ascribed to the fact that only the fraction 10^{-5} to 10^{-8} of the surface is active. This small number of active points supports the explanation of the "flat part" of the isothermals, mentioned in Part I.

The figures in Table II. are given in the order in which they were obtained, except that the fourth experiment at 579° K. was carried out after all the others, to test if the activity of the palladium had changed. In spite of a temporary admission of air (followed by evacuation and washing with H_2) before this experiment, the value of a is in good agreement with former experiments. The palladium at 373° K. showed abnormal activity and absorbed hydrogen with great rapidity.

Experiments at 100° C.—These experiments show that the flat part of the curve is superimposed on an almost linear adsorption isothermal, and is not obtained when the amount of hydrogen which has entered the lattice is small. The sequence of experiments at 100° C. can be followed from the three sets of curves a , b , and c in Fig. 2. [Capillary (I.) $K = 2.02 \times 10^{-7}$ moles/min.; capillary (II.) $K = 8.09 \times 10^{-7}$ moles/min.]

Fig. 2a.—*Curve (I.)*.—Open to hydrogen reservoir for $t_1 = 25$ mins. Time (t_2) the system is allowed to absorb and reach more or less steady state with tap shut, 70 mins. (a drop of pressure of about 1.2 cms. occurs during the time). (Cap^v. I.)

Curve (II.).—Air let in. Evacuated. Repeatedly washed with hydrogen. $t_1 = 16$ mins., $t_2 = 12$ mins.

Curve (III.).—Similar circumstances as for Curve (II.). $t_1 = 32$ mins., $t_2 = 60$ mins.

For Curve (II.) Fig. 2a, the "flat part" is shorter than for Curve (I.); as less hydrogen has been absorbed. The other parts of the isothermal are roughly parallel (but the pressure of the "flat part" is slightly higher probably owing to the temperature control for Curve (I.) being unsatis-

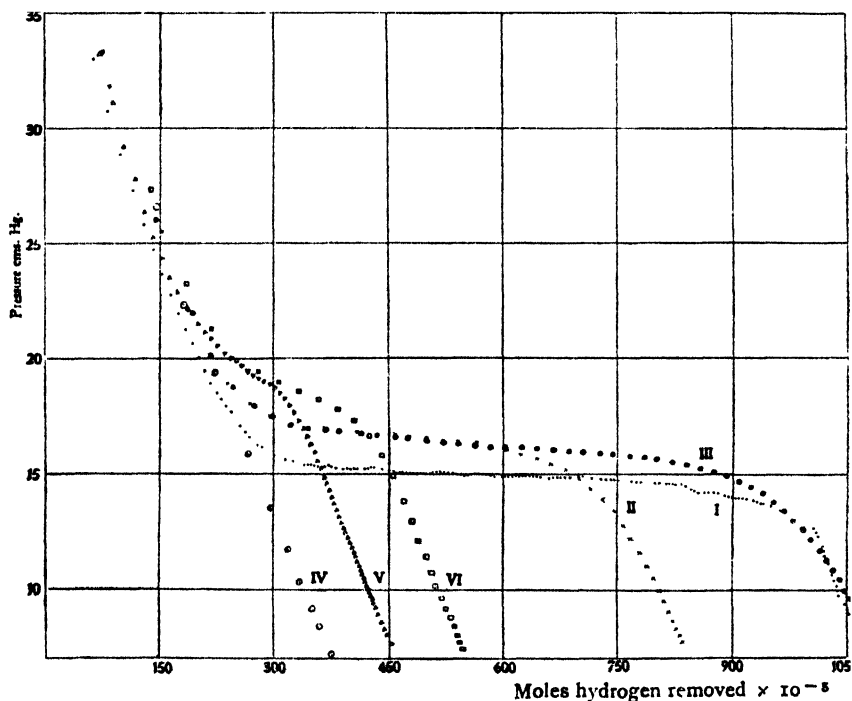


FIG. 2a.

factory). In the case of Curve (III.) more hydrogen had been absorbed, the first and third branches of the isothermal are again roughly parallel. The only effect of adding more hydrogen is to extend the "flat part."

The average slope of the "flat part" in Curve (I.) is about 1 cm. for 6×10^{-3} moles, which is about 1.5 times the slope of the "flat part" obtained by Lambert and Gates³ in their equilibrium isothermals. For Curve (II.) with the faster rate of removal the slope is about 3.5 times as large, but when more hydrogen is absorbed (Curve (III.)) the slope is less, and the rounding off at the end is less abrupt.

It is not difficult to interpret these results in terms of the explanation of the "flat part" already given. As long as the rate of removal of hydrogen is small compared with the rate at which atoms can diffuse from the interior to the surface, the pressure will remain practically constant. As the concentration of the hydrogen in the interior gets less,

the rate of diffusion gets less, and the pressure drops at first gradually, then more rapidly. The point at which this occurs will depend on the amount of hydrogen *initially* present.

Curve (IV).—Hydrogen added immediately after obtaining Curve (III.), $t_2 = 20'$ (Cap^v. II.). Tap shut each three or four minute intervals for ten minutes to test whether pressure changed if more time was given for equilibrium.

A straight line was obtained. ($L = kp$ where $k = 2.83 \times 10^{-5}$ moles/grm.).

Curve (V.) $t_1 = 19'$ $t_2 = 60'$ (Cap^v. II.),
Curve (VI.) $t_1 = 18'$ $t_2 = 180'$ (Cap^v. I.).

It is clear that before experiment IV. the palladium had been completely poisoned. This makes little difference to the first and third part of the isothermal, but the "flat part" is either missing or very much reduced. Before the minute crack which was the cause of this poisoning was noticed, an attempt was made to reactivate the palladium by alternate washing with air and hydrogen, followed by evacuation at 100° C. Curve (V.) follows on this treatment, and shows that a small activity had been restored. (The "flat part" begins at a somewhat higher pressure, but this is probably due to a small partial pressure of nitrogen in the vessel. The effect is not observed when oxygen alone is used for the poisoning.) The constant small leak of air soon re-poisons the palladium, however, and practically no "flat part" appears after even three hours' contact with hydrogen (Curve (VI.)). The slope of the lowest part of the isothermals (IV.), (V.), and (VI.) is the same, and is somewhat greater than for Curves (I.), (II.), and (III.). The curves in Fig. 2a support the view that the removal isothermals of palladium/hydrogen³ are due to weak surface adsorption proportional to the pressure, with a large solubility curve superimposed. When there is sufficient hydrogen in the lattice the slope of the third part of the isothermal is also less, as would be expected.* Poisoning makes little or no difference to the slope of the first part of the isothermal, which supports the view that no hydrogen leaves the interior of the lattice before the "flat part" is reached, *i.e.*, that the hydrogen in the lattice exerts a definite saturation pressure, and only leaves the lattice if the applied pressure is smaller than this.

Fig. 2b.—*Curve (I.).*— t_2 18 mins.—A repetition of the previous experiments before the crack which allowed a small trace of air to enter was noticed. A trace of water was then observed inside the reaction vessel.

The palladium was transferred to a new vessel evacuated at 306° C., and washed with H₂.

Curve (II.).— t_1 20 mins., t_2 30 mins. Capillary (II.).—The palladium had recovered considerable activity, giving a "flat part" in the isothermal.

Curve (III.).—Oxygen at 2 cms. pressure added (from KMnO₄ and purified). Heated again, and H₂ added; t_2 38 mins. (Apparent mass occluded too large owing to no allowance made for viscosity of oxygen.)

* When some hydrogen is absorbed this slope is the same as for poisoned palladium. If hydrogen had entered *all* the granules, the slope would be the same as for active palladium. Hence partial activation involves complete activation of a few granules leaving the rest poisoned.

Curve (IV.).—Heated in H_2 306° for 20 mins. Cooled to 100° , and partly evacuated; t_2 9 mins. Amount absorbed still small.

Curve (V.).—Heated in H_2 306° for 20 mins. Cooled and H_2 added without evacuation; t_2 35 mins. Oxygen poisoned the surface of the palladium and it had not recovered activity by this treatment.

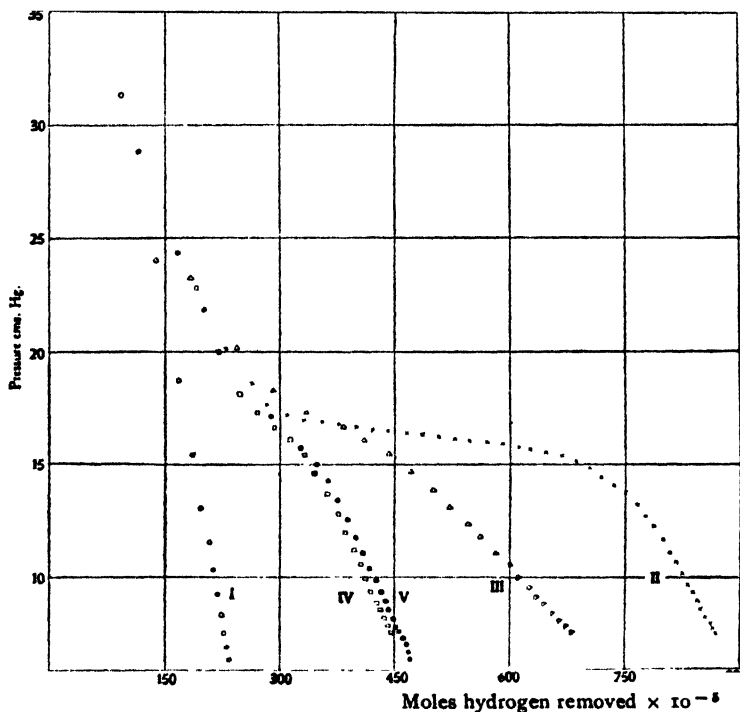


FIG. 2b.

Fig. 2c.—*Curve (I.).*—Heated in hydrogen, t_1 120' without evacuating subsequently; t_2 35', still poisoned.

Curve (II.).—Evacuated thoroughly at 306° C. washed with hydrogen, evacuated at 100° ; t_2 15 mins. Activity recovered by this treatment.

Curve (III.).—Hydrogen let in up to lower initial pressure (26 cms.), t_2 10 mins.

Curve (IV.).—Hydrogen let in to higher initial pressure (32 cms.), t_2 30 mins.

Curve (V.).—Repeat of (III.). (Curve (IV.) also confirmed, but not shown.)

Curve (VI.).—Oxygen (pure) again added at 100° to 10 cm. pressure after evacuating. Heated for 10', oxygen pressure reduced to one or two millimetres. H_2 added (30 cms.); t_2 15 mins. This treatment poisoned the palladium again partially.

Curve (VII.).— H_2 added to 30 cms. and t_2 15 mins. Activity recovered. These experiments showed that only when sufficient time is allowed, and the initial pressure is high enough, will the hydrogen enter the lattice sufficiently to provide a "flat part" in the curve, otherwise not enough has been absorbed, and very slight change of slope, if any, is observable (see Curves (III.) and (IV.)). They also showed that oxygen

poisons the surface and only after considerable heating in hydrogen can the activity be recovered (see Curves (VI.) and (VII.)).

The result shown on Curves (VI.) and (VII.) should be contrasted with the previous oxygen poisoning (Fig. 2*b*, Curve (III.)), where the palladium could only be reactivated after thorough evacuation. The difference between the two experiments was that in the first the palladium was not evacuated before adding oxygen, and the amount of oxygen added in the presence of hydrogen was larger. The origin of the poisoning is most probably the oxidation of the active points, and in the presence of sufficient water vapour, such as would be present in the reaction vessel before evacuation, the reaction $\text{PdO} + \text{H}_2 = \text{Pd} + \text{H}_2\text{O}$ cannot proceed to completion. Further experiments are being made to investigate this point. The fact that moisture does not affect the

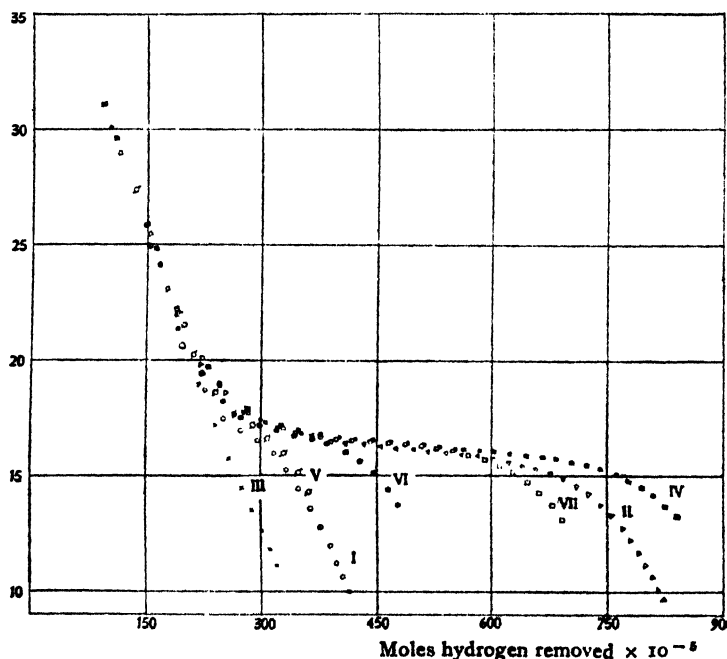


FIG. 2c.

rate of adsorption at 0°C .³⁵ does not contradict the above view, since the equilibrium would be much more slowly reached at this temperature.

The initial reduction of copper oxide³⁵ is inhibited by water vapour, the progressive reduction by oxygen. Similar effects with palladium may explain why oxygen inhibits the reaction $\text{H}_2 \rightarrow 2\text{H}$ and why water prevents re-activation.

Although Hoitsema showed the existence of the "flat part" of the isothermal so long ago as 1895, and Ramsay, Winkelmann and others have given evidence for the dissociation of hydrogen into atoms in diffusing through palladium, the significance of the activity of the surface in controlling the rate of entry, and influencing the character of the isothermals on addition or removal has not been made sufficiently clear. As elaborated in Part I., entry is difficult because dissociation has first to be effected at the surface, and depends on the activity of the

surface, but removal is very much easier because the reaction $2\text{H} \rightarrow \text{H}_2$ is so much more rapid. Similar mechanisms will probably hold for solution in metal lattices in general.*

Summary.

The removal isothermals were determined at 306° , 218° , 156° and 100°C . A single value for α , the fraction of the impinging molecules adsorbed, is calculated for each temperature, and the relative influence if the activation energy and number of active points per cm^2 on α is determined. A "flat part" of the isothermals was only observed at 100°C ., and by varying the activity of the palladium or the time of exposure to hydrogen the "flat part" can be both completely eliminated or made to approach the maximum value observed by Lambert and Gates.²

The results afford further support for the views advanced in the theoretical discussion.

* It is clear that an activation process is required before hydrogen will enter palladium. The observation recorded in the footnote on page 288 and other evidence (e.g. 32, 23) indicates that when a certain amount of hydrogen has entered a granule, further entry is much more rapid, i.e. the activation required is much smaller. This is probably connected with the expansion of the lattice giving a more favourable separation distance of Pd atoms for the catalysis of the reaction $\text{H}_2 \rightarrow 2\text{H}$. In a metal wire the "grains" correspond with the granules in our experiments, and once hydrogen enters a given grain the complete saturation of that grain rapidly follows, without the hydrogen being able to cross the distorted lattice at the boundary of one grain and the next. This would explain the fact that two "phases" are apparently obtained side by side in some X-ray experiments (32). Until it has been shown that two "phases" are obtained side by side even when a single crystal of palladium is used initially, it seems safer to adopt the above explanation, according to which the slowness of equilibrium between one grain and the next gives the appearance of two phases. The adsorption in the grains seems to be autocatalytic.

KINETICS OF ADSORPTION PROCESSES. III. THE INFLUENCE OF NUCLEAR SPIN ON THE SORPTION OF HYDROGEN ON CHARCOAL.

By A. R. UBBELOHDE, B.A., B.Sc.

Received 7th December, 1931.

The potential of a molecule usually changes as it approaches a boundary between two phases, owing to the presence of forces causing adsorption. In some cases these forces are much larger than the van der Waals forces between the molecules of the sorbate. Hydrogen, for example, is adsorbed in comparatively large amounts on charcoal at fifty degrees or more above the critical temperature, and the heat of adsorption is about twenty times as large as the latent heat of vaporisation.

Bonhoeffer and Harteck¹ showed that liquid para hydrogen has a higher vapour pressure than the ordinary mixture of 75% ortho and 25% para hydrogen. The experiments to be described in this communication were undertaken in order to try and find out whether the two spin isomers showed any difference in behaviour under the influence of the large forces causing the adsorption of hydrogen.

Active charcoal is a catalyst¹ at low temperatures for the reaction $\text{H}_2(o) = \text{H}_2(p)$, and before the mechanism of this heterogeneous reaction

can be elucidated, it is necessary to know the relative adsorption of the two isomers. If C_1 and C_2 are the equilibrium concentrations of the two isomers in the gas phase, $C_1/C_2 = K$, where K is a function of temperature only.^{1, 2} At any given temperature and pressure the adsorbed molecules will also be in equilibrium, but unless the work of adsorption of each isomer is the same, the ratio $c_1/c_2 = r$ in the adsorbed layer will in general be different from K . Since the presence of the catalyst cannot alter the equilibrium in the gas phase, r can only be different from K if the velocities of adsorption and evaporation of the two isomers are different. When gas is removed from the adsorption vessel, the equilibrium mixture will always be obtained if the removal is sufficiently slow, owing to the presence of the catalyst. As the rate of removal increases, any difference between the velocities of evaporation will begin to influence the composition of the gas, even if the temperature is kept constant.

The dynamic equilibrium in the adsorption vessel is set up as follows: the rate at which molecules of *ortho* hydrogen condense on the charcoal will be $C_1 a_1 k$, where k is a constant obtained from the kinetic theory of gases, and a_1 is the fraction of the impinging molecules that passes into the adsorbed state. The rate of evaporation will be $c_1 v_1$. At equilibrium, $C_1 a_1 k = c_1 v_1$, and for *para* hydrogen $C_2 a_2 k = c_2 v_2$. If activation is required for adsorption, $a_i = e^{-E_i/RT}$, and $\ln a_1 k - \ln v_1 = \phi/RT$, where ϕ is the adsorption potential. For hydrogen on charcoal, the activation required for adsorption may be assumed small compared with ϕ (cf. 3), and a_i is practically unity. The equations for equilibrium in this case are

$$C_1 k = c_1 v_1 \text{ and } C_2 k = c_2 v_2, \\ c_1 v_1 / c_2 v_2 = C_1 / C_2 = K \quad . \quad . \quad . \quad (1)$$

If no reversion to equilibrium takes place during the removal of the freshly evaporated gas, its composition may be estimated as follows:—

During the removal,

$$dc_1/dt = -v_1 c_1 \text{ and } dc_2/dt = -v_2 c_2$$

if c_1' and c_2' are the initial concentrations, the values of c_1 and c_2 after any time t will be related by

$$(1/v_1) \ln (c_1/c_1') = (1/v_2) \ln (c_2/c_2') \quad . \quad . \quad . \quad (2)$$

The composition of the freshly evaporated gas will be $\Delta c_1/\Delta c_2$, if Δc_1 and Δc_2 are the numbers of molecules of each type actually evaporated.

Equation (2) is equivalent to

$$(1/v_1) \ln (1 - \Delta c_1/c_1) = (1/v_2) \ln (1 - \Delta c_2/c_2).$$

When Δc_1 and Δc_2 are small compared with c_1 and c_2 , only the first term of the logarithmic expansion need be retained, and

$$\Delta c_1/\Delta c_2 = c_1 v_1 / c_2 v_2 = K.$$

The freshly evaporated gas thus approximates closely to the equilibrium mixtures. When the amounts of gas removed are larger, relative to the total amount adsorbed, the first two terms of the expansion will be of importance, and

$$1/v_1 \Delta c_1 / c_1 (1 + \Delta c_1 / 2c_1) = 1/v_2 \Delta c_2 / c_2 (1 + \Delta c_2 / 2c_2)$$

$$\text{whence} \quad 1/K \Delta c_1 / \Delta c_2 = \frac{1 + \Delta c_2 / 2c_2}{1 + \Delta c_1 / 2c_1}$$

$$\text{and} \quad \Delta c_1 / \Delta c_2 \geq K$$

according as $1 + \Delta c_2/2c_2 \gtrless 1 + \Delta c_1/2c_1$,

i.e. $c_1/c_2 \gtrless \Delta c_1/\Delta c_2$.

Hence either $c_1/c_2 > \Delta c_1/\Delta c_2 > K$,

or $K > \Delta c_1/\Delta c_2 > c_1/c_2$.

The composition of the freshly evaporated gas will thus be intermediate between the equilibrium mixture in the gas phase, and that in the adsorption layer. When the mass of adsorbent is kept small, so that the displacement from equilibrium is sufficiently large, analysis of the freshly evaporated gas will give qualitative information as to which spin isomer is the more adsorbed.

For hydrogen on charcoal, two factors may affect the relative adsorption of the two isomers. From its lower vapour pressure, the average deformability of *ortho* hydrogen along the different axes would seem to be greater than that of *para* hydrogen, so that a greater adsorption would be expected. A subsidiary factor which may be of considerable importance for the difference in behaviour of the two spin isomers is the rotational state of the adsorbed molecule.³ If the polarisability of the molecule is different along the different axes, the more firmly bound molecules may no longer possess enough rotational energy to be able to complete a rotation. These molecules will oscillate about a mean position. The calculation for an analogous problem in crystals⁴ may be applied here; if W is the rotational energy, and V_0 the function relating the adsorption potential of the molecule with its orientation, the molecules will rotate or oscillate according as

$$W \gtrless 2V_0.$$

Both the lateral forces between adsorbed molecules and the forces directed towards the surface will decrease when the molecule rotates, and the transition between a system with most of the molecules oscillating, and one where most of the molecules rotate is complete in a fairly narrow range of temperatures.⁴ An adsorbent like charcoal probably contains regions of different adsorption potential, decreasing continuously from very high values, at points where the valency bonds of the carbon atoms are unsaturated, to fairly low values in regions where the lattice is merely distorted. The points of high adsorption potential will be occupied even at low pressures, and as the pressure increases the regions of lower adsorption potential will gradually be filled. For such an adsorbent, even at constant temperature, there will be a region of critical adsorption potential above which all the molecules oscillate, and below which they rotate.

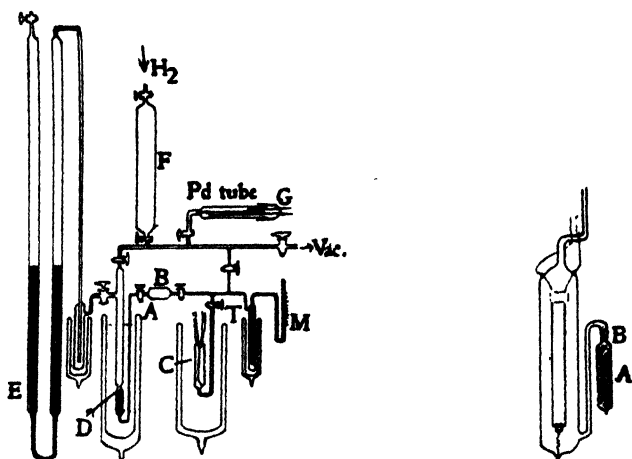
This critical region will be different for each successive rotational quantum; if the change over from rotation to oscillation is complete in a narrow region of pressures, the adsorption isothermal will show a series of small discontinuities. Sudden changes of slope in the isothermals have actually been observed,^{5, 6} though a somewhat different explanation has been offered.

In cases where a reaction such as $H_2(o) = H_2(p)$ takes place on the surface, the lateral forces between the adsorbed molecules must be fairly large, and a fairly abrupt change in adsorption potential will take place in passing through the critical region. If heterogeneous catalysis is to be explained⁷ as due to longer contact of adsorbed molecules, rotating

molecules will be at a disadvantage, since they are less firmly held, and since they cannot remain in the most favourable orientation for reaction. For the system hydrogen/charcoal, the relative adsorption of the two isomers may be different at different pressures, and the rotational state may influence the velocity of the heterogeneous reaction.

Experimental Methods.

The principle of the experiments was to test for a difference in composition between the freshly evaporated gas and the equilibrium mixture at the same temperature. A small mass of active charcoal was saturated with hydrogen, and the gas was rapidly pumped off after allowing sufficient time for equilibrium to be established. Any change in composition is detected from a change in the thermal conductivity of the gas. However small the charcoal granules are, at least 50 per cent. of the space they occupy will not come under the influence of the adsorptive forces, and will contain the gas equilibrium mixtures. The gas from this free



FIGS. 1 and 2.

space dilutes the freshly evaporated gas, and lessens the change in composition. It is therefore necessary to make the apparatus as sensitive as possible to changes in thermal conductivity. The gauge for measuring thermal conductivities was immersed in a cryostat⁶ maintained at about -120°C. , at which temperature the difference between the specific heats of the two isomers passes through a maximum, and the thermal conductivity also shows a larger difference than at other temperatures. (The two maxima will only coincide if the ratio of the viscosities remains constant . . . *cf.*³)

The hydrogen was prepared by electrolysis.³ The purity was checked (*cf.* Fig. 3, A and B) by comparison of thermal conductivity with that of hydrogen diffused through a palladium tube (G in Fig. 2), the measurements being made under similar conditions. Fig. 1 shows the general arrangement of the apparatus. The vessel D (shown in detail in Fig. 2) is filled with about 2 gm. of active nut charcoal, up to the constriction; the volume of D is about 2 c.c. and of the dead space above D about 15 c.c. The charcoal in D is heated to 440°C. and evacuated, then washed with pure hydrogen at the temperature of liquid oxygen; this process is

repeated two or three times, to make sure that no impurity remains in the charcoal that can be displaced by hydrogen at the temperature of liquid oxygen. Hydrogen is then passed into the vessel till the pressure is about 60 cm. Hg, and the taps to the manometer E and reservoir F are shut. Liquid oxygen covers the charcoal in D and about two-thirds of the dead space above. The system is left for an hour or more to come to equilibrium, and samples of gas are then transferred at suitable intervals to the evacuated gauge C by means of the tap A. The volume B serves to remove smaller masses of gas from the charcoal, when this is necessary.

The gauge wire was thin tungsten about 3 cm. long mounted axially in a tube. The tube was filled with the gas to be investigated, and after reducing the pressures (read on the manometer M) to about 5 cm. the tap T was shut and a current was passed through the gauge wire. The resistance of the gauge was about 0.7 ohm, and the resistance and current (about 0.4 amp.) were determined by measuring the potential drop (to 0.2 millivolt) across the wire and across a standard ohm in series with it.

The temperature of the bath was measured to 0.05° C. by means of five copper constantan couples in series, using a sensitive micro-ammeter. When a more sensitive means of measuring temperature was required the gauge wire itself was used as resistance thermometer, using small currents.

In these experiments the current through the wire remained practically constant. If the bath temperature is kept constant the equilibrium resistance will be higher the lower the thermal conductivity of the gas. The wire does not reach temperature equilibrium immediately, so that the resistance was measured after two fixed intervals of time, and the further small change neglected. In Fig. 3 the resistance of the gauge wire is plotted against the time of removal from the charcoal. The values are corrected for the slight change of resistance of the wire with change in pressure and temperature, using empirically determined corrections.

In Fig. 3, Expt. A, the hydrogen had been in contact with the charcoal 330 minutes before beginning withdrawals. The point (a) differs from the others in that a tap was opened so that hydrogen could stream over the charcoal and into the gauge. In Expt. B 98 minutes' contact were allowed before beginning withdrawals. The point (a) has a similar history to that in Expt. A, and (b) was preceded by three rapid removals of gas. The upper points in the two figures show check values with ordinary hydrogen from the reservoir, and in Expt. A also with the hydrogen diffused through palladium.

The fluctuations in composition of the freshly evaporated gas were greater than the estimated error of measurement. They were larger

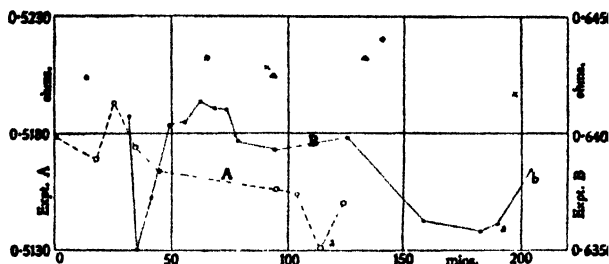


FIG. 3.

Δ H_2 (from Pd) } Experiment A.
 * H_2 (electrolytic) }
 x H_2 " } Experiment B.

than variations in temperature of the liquid oxygen bath would produce, and were not due to cooling of the charcoal when H_2 is removed, since on repeated removal at short intervals more *ortho* H_2 was obtained, whereas cooling would only produce more *para* H_2 . These experiments were repeated a number of times, and when the amount of charcoal is increased more gas has to be pumped off in order to get a comparable increase in *ortho* H_2 . This shows that fluctuations are not due to chance reversion along the connecting tubes. The passage of the gas through these is rapid. The magnitude of the effect might be different for different samples of active charcoal.

The time of contact allowed before beginning the experiments was ample to bring the hydrogen to equilibrium, so that the change in composition of the freshly evaporated gas can only mean that the two spin isomers were not adsorbed to the same extent. The presence of more *ortho* hydrogen in the freshly evaporated gas indicates that most probably (unless the fractions a (*vide supra*) are very different) *ortho* hydrogen is more strongly adsorbed than *para* hydrogen in this region, in agreement with the vapour pressures.

The only regularity that could be observed was that the amount of *ortho* hydrogen increased when the gas was removed at brief intervals, without allowing time for the dead space gas to revert to the equilibrium mixture. In these experiments the pressure of hydrogen over charcoal fell from 60 to 5 cm. (Some evidence was obtained that the gas evaporated at still lower pressures was richer in *para* hydrogen. This is probably due to the smaller displacement of equilibrium at these pressures, where the mass of gas removed is smaller.)

Measurements were also carried out with the charcoal bulb sealed off at the constriction (*cf.* Fig. 1) after evacuation, to see if the variation in *ortho* hydrogen could be correlated with the equilibrium pressure over the charcoal. Maxima and minima were obtained on the curve of composition plotted against equilibrium pressure, but could not be reproduced at the same pressures (± 1 cm.) in the different experiments.

With the above method, it was impossible to obtain results that could be quantitatively reproduced, since the hydrogen removed from the reaction vessel consisted partly of gas from the dead space (at least 50 per cent. of the bulk of the charcoal) which would be at the theoretical equilibrium mixture at the temperature of liquid oxygen, and partly of freshly evaporated gas, which contained more *ortho* hydrogen. The relative amounts depend upon the rate of removal, and it is not possible to secure a constant rate of removal by opening a tap to the evacuated gauge.

An attempt was made to overcome these difficulties by removing the gas continuously from the charcoal, and passing it through the gauge. The whole system was immersed in the same liquid oxygen bath, so that no error could arise from the connecting tubes. A long thin bulb (see Fig. 2) contains about two grams of charcoal. As before, it is heated in boiling sulphur and evacuated, then washed with hydrogen at -183° C., the treatment being repeated several times. A constriction at B, and a little glass wool fixed in the constriction, prevent any charcoal particles from entering the gauge by convection. The gauge consists of two fine platinum wires, held in position parallel to the axis of the tube by a small glass hook at the bottom, and weakly stretched by a coil of glowed platinum wire. Platinum was used in place of tungsten, as with tungsten the reaction $H_2(o) = H_2(p)$ is slowly catalysed at low

temperatures. In order to minimise convection, which is more serious in a streaming method, the internal diameter of the gauge was only 1 cm. The wires were 3 mm. apart and 6 cm. long, and the total resistance at -183°C. was about 2.56 ohm. The resistance was measured on a Callendar Griffiths bridge, reading to 0.0001 ohm; the sliding contact was locked at a given point, and the change in resistance calculated from the deflection of a galvanometer, previously calibrated in terms of the slide wire.

The gauge and charcoal were isolated from the rest of the apparatus by a wide tap and a mercury vapour trap. Before beginning an experiment, hydrogen was admitted to the vessel up to a pressure of about 30 cm., and left for an hour or more to come to equilibrium. A tap connecting the system to a suitable capillary which controlled the rate of evacuation was opened after adjusting the setting of the Callendar bridge. Readings of the galvanometer spot were taken every half-minute or minute, and the manometer was read at intervals. From these readings a curve could be constructed showing the change of resistance as the pressure over the charcoal dropped. Blank experiments were made under the same conditions, but with the charcoal sealed off, so that the composition of the hydrogen remained constant. The resistance at a given pressure obtained from the blank experiments was subtracted from the resistance observed in the presence of the charcoal. This eliminated nearly all the corrections due to convection, etc., and the remaining corrections, such as that due to the lag of the temperature of the platinum wire behind the equilibrium temperature, were not sufficient to obscure any change in conductivity of the gas from the charcoal. Capillaries of different resistances were used, in order to secure different rates of removal. At low rates of removal, the reversion of the freshly evaporated gas to the equilibrium mixture is considerable. If too fast a rate of removal is used, the resultant cooling of the charcoal produces disturbances in the composition of the freshly evaporated gas, and any discontinuities in the pressure/resistance curve will be blurred.

In these experiments it was not possible to avoid irregular movements of the galvanometer spot, owing to irregular mixing in the gauge and uncompensated thermo-electromotive forces. These oscillations are superimposed on a uniform movement in any direction. In order to reduce them to a minimum, the charcoal bulb was surrounded by copper gauze, to equalise its temperature, and the gauge was kept well below the level of the liquid oxygen. Compensating leads were introduced in the second arm of the Callendar bridge. These were similar to the main leads, and were joined in the liquid oxygen bath by a length of platinum wire similar to that used for the main leads. The number of readings is so numerous that a smoothed curve can be drawn through the points with considerable certainty (average departure from smooth curve 0.0001 ohm).

Fig. 4 shows a typical curve of the *difference* of resistance in presence and in absence of charcoal, plotted against the pressure, together with the blank experiment for which resistance is plotted against pressure. The slight fall at the higher pressures is probably not due to increasing amounts of *ortho*, but to an uncorrected decrease in cooling of the wire as the stream gets slower. Occasional maxima and minima were observed in other curves, particularly at faster rates, but these could not be reproduced at the same pressure. The maximum at 13 cm. shown in Fig. 4 occurs at the same pressure on two curves for the same capillary. All the curves show that the difference in resistance became larger at

lower pressures, indicating more *para* hydrogen. This increase in the amount of *para* hydrogen at low pressure, as already stated, is probably to be explained as due to the slower rate of removal.

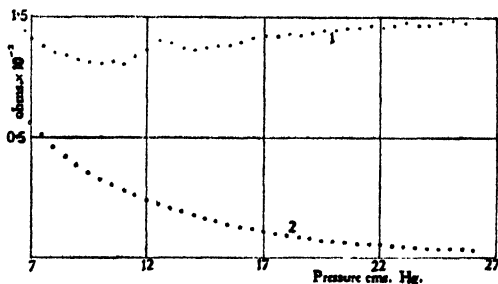


FIG. 4.

Curve 1.—Difference of resistance with and without charcoal.

Curve 2.—Blank experiment resistance change with pressure.

($K = 1.2, 10^{-7}$ mole/min. at 1 cm. Hg.)

are different. It implies that hydrogen molecules retain their identity when adsorbed on charcoal. This makes a mechanism of reaction $H_2(o) = H_2(p)$ by way of atoms¹ unlikely in the adsorbed phase. The reaction might possibly take place between two adsorbed molecules interchanging atoms, or by impact of a molecule from the gas phase on to a deformed hydrogen molecule.

These experiments were made in consultation with Mr. Egerton, F.R.S., in the Clarendon Laboratory, Oxford.

Summary.

When suitable precautions are taken to prevent reversion, the gas freshly evaporated from charcoal at the temperature of liquid oxygen contains more *ortho* hydrogen than the equilibrium mixture. The most probable interpretation of this result is that *ortho* hydrogen is more adsorbed than *para* hydrogen at the temperature of liquid oxygen. No definite change in relative adsorption could be found (within 1 per cent.) when hydrogen is continuously removed over the range of pressures 2.5–7 cm.

Note.—There seems to be no reason why the adsorption of the two spin isomers should be the same at high temperatures, though the increasing rotation of the molecules might obscure any difference. This was tested with palladium over a range of temperatures from 300 to 100° C.; the hydrogen was removed continuously and passed through the gauge at the temperature of liquid oxygen. The fluctuations in composition were definitely about twice as large as the difference between two blank experiments, but were not always reproducible. This may depend on the surface of the palladium, which is very sensitive to poisons. An alternative explanation is (*cf.* ⁷) that a number of the H_2 molecules leave the metal surface as ions (H_2^+), which may persist in the charged state for a certain length of time, and lead to an increase in the *para* hydrogen in the gauge at -183° C. Other adsorbents have not yet been tried by this method.

REFERENCES.

- ¹ K. Bonhoeffer and P. Harteck, *Z. physik. Chem.*, **4B**, 113, 1929.
² W. Giauque, *J.A.C.S.*, **52**, 4816, 1930.
³ Ubbelohde and Egerton, *Proc. Roy. Soc.*, **134**, 512, 1931.
⁴ L. Pauling, *Physic. Rev.*, **36**, 431, 1930; T. Stern, *Proc. Roy. Soc.*, **130A**, 551, 1931.
⁵ A. Allmand and L. J. Burrage, *Proc. Roy. Soc.*, **130A**, 610, 1931.
⁶ Egerton and Ubbelohde, *Farad. Trans. Soc.*, **26**, 1930.
⁷ K. Bennewitz and F. Gunther, *Z. physik. Chem.*, **111**, 257, 1924.
⁸ G. von Elbe and F. Simon, *Z. physik. Chem.*, **6B**, 79, 1929.
⁹ M. Born and V. Weisskopf, *Z. physik. Chem.*, **12B**, 106, 1931.

THE EXPLOSIVE COMBINATION OF HYDROGEN AND OXYGEN—THE FUNCTION OF WALLS IN GASEOUS REACTIONS.

By H. W. THOMPSON.

Received 17th December, 1931.

From the variety of examples examined during the past few years it has become certain that many chemical processes occurring thermally involve the production of reaction chains, which are of essentially the same nature as those previously supposed to play a part in certain photochemical changes. The more precise nature of such reaction chains, and their mode of production, propagation, and stoppage in thermal processes, has been a subject for subsequent investigation.

It is as yet uncertain whether these chains are of a "material" or "energy" type, *i.e.*, whether their continued propagation depends upon the production of new chemical species or simply upon the transfer of surplus energy from product molecules to those of the reactants. Notwithstanding this the chains appear to fall into two classes, which have been differentiated by the terms "straight" and "branching." Whereas the straight chains in general lead to a measurable reaction velocity, branching chains are apparently inevitably accompanied by ignition. Further, since comparatively small changes in pressure are known to produce noticeable changes in the tendency of chains to branch, it will not be surprising to find that a measurable and slow combination may, with slight alteration in experimental conditions such as pressure, become an explosive one. Examples of this phenomenon are now common.¹

Despite advances of this type in our knowledge of the nature of reaction chains, our understanding of their origin and stoppage, and to a less extent of their propagation, is in an unsatisfactory and entirely empirical state. In investigations of the velocity of straight chain processes it has been found that a decrease in dimensions of the reaction vessel markedly cuts down the rate, and this is now tacitly applied as a criterion of such chain mechanisms. In other words the reaction chains are being broken on the wall. There are other cases in which

¹ See Hinshelwood, "Kinetics of Chemical Change," 2nd edn. Chap. VI.; Semënov, *Chemical Reviews*, VI., 3, 1929.

reaction chains are undoubtedly broken in the gas. The method by which such reaction chains are produced is, however, much less clear.

This inadequate knowledge of the origin and destruction of reaction chains makes any fresh evidence which can be regarded as conclusive very important. The results to be outlined in the following appear to make it definite that when reaction centres are introduced into a mixture of hydrogen and oxygen in the body of the gas, the progress of the combination, *i.e.*, the propagation of the chains, depends upon the rate at which these chains can reach the vessel walls. Addition of inert gases to the mixture can increase the ignitability of hydrogen-oxygen mixtures at low pressure presumably by preventing a rapid diffusion of the active centres to the vessel walls. The mechanism by which such active centres are destroyed at the walls is not yet known, but it seems certain that it is by a chemical reaction with adsorbed gas molecules. The report now submitted is of a preliminary nature: a more careful study of the relationships involved is now in progress from which it is hoped to find by kinetic theory considerations what the active centres in the hydrogen-oxygen chain are. The present experiments were all carried out at room temperature; variation of the temperature up to 400° C. will very probably help in this connection.

It is known that hydrogen-oxygen mixtures explode at relatively low pressures at 500° C. if the total pressure is between two sharply-defined limits. Outside these limits the combination is in general slight.² The relationships involved at the upper limit could be investigated by the method described by Thompson and Hinshelwood;² it appeared that a "gas" deactivation process was most important here, and a hypothetical mechanism for a chemical gaseous chain breakage was suggested. Alyea and Haber have also examined this problem by another method.³ The discussion of their work may be found elsewhere.⁴

The study of the lower limiting pressure of the critical explosion region of hydrogen and oxygen was not made by Thompson and Hinshelwood for experimental reasons. Kopp, Kowalsky, Sagulin and Seménov who regarded it as a so-called "*Restdruck*," concluded that it was either completely or almost independent of the vessel dimensions, and in the presence of argon the partial pressure of the hydrogen plus oxygen at the limit remained constant over the range 0.60 per cent. argon. The limit is, however, situated at such a region of pressure that its investigation by the methods originally used are somewhat difficult, and the results thereby obtained are accordingly to be regarded as approximate.

A convenient method of investigating the influence of various factors upon the lower limit has recently been discovered. Stavenhagen and Schuchard⁵ discovered some years ago that when hydrogen-oxygen mixtures at room temperatures are exploded by a spark, they fail to ignite if the pressure falls below a critical value. Alyea and Haber have correlated this limit of the propagation of the explosion wave in the gas at ordinary temperatures with the lower limit of Thompson and Hinshelwood at higher ones. According to Alyea and Haber reaction

² Thompson and Hinshelwood, *Proc. Roy. Soc.*, **122A**, 610, 1929; Kopp, Kowalsky, Sagulin, Seménov, *Z. physikal. Chem.*, **6B**, 307, 1930.

³ Alyea and Haber, *Z. physikal. Chem.*, **10B**, 193, 1930.

⁴ Garstang and Hinshelwood, *Proc. Roy. Soc.*, **130A**, 640, 1931; *ibid.*, **134A**, 1, 1931.

⁵ Stavenhagen and Schuchard, *Z. angew. Chem.*, **33**, 286, 1920.

chains starting on the wall, will, at a pressure just greater than the lower limit, be adequately propagated in the gas to produce the type of chain which results in ignition. This assumption is somewhat arbitrary, and further, since in the experiments of Stavenhagen and Schuchard the active centres originated in the gas, the mechanism suggested by Alyea and Haber cannot be drawn by analogy. The main point was first to discover whether the critical explosion pressure with a spark really varied with the temperature in such a way that when extrapolated to the temperatures of Thompson and Hinshelwood it coincided with their values for the lower limit. From experiments of Haber and of Kowalsky⁶ this would appear to be the case, although the investigations of Finch might suggest that the absolute value of the critical pressure limit will depend upon the intensity of the spark used.

Assuming, however, that the critical explosion pressure with a spark is the same in principle as that originally described by Thompson and Hinshelwood, the influence of various factors such as the addition of inert gases, the ratio $H_2 : O_2$, and the temperature can easily be investigated.

Melville and Ludlam⁷ have recently examined the influence of inert gases upon the lower critical limit in the oxidation of phosphorus vapour, and Dalton and Hinshelwood⁸ investigated the lower limit in the oxidation of phosphine in a similar way. According to the original theory of Semënov, assuming that the chains break at the wall, for any given temperature the following relationship holds at the limit :

$$p_{P_2} p_{O_2} \left(1 + \frac{p_{\text{inert gas}}}{p_{P_2} + p_{O_2}} \right) d^2 = k,$$

d being the vessel diameter. Semënov⁹ had previously shown that as regards vessel size this equation was adhered to, and in the presence of argon plotting $\frac{1}{p_{P_2} p_{O_2}}$ against $\left(1 + \frac{p_{\text{inert gas}}}{p_{P_2} + p_{O_2}} \right)$ a straight line was obtained. Employing different inert gases Melville and Ludlam obtained a series of straight lines of this type. The interesting feature lies in the difference of slope of these lines, which changes uniformly from the least complex to the most complicated of the molecules used. The suggestion made was that the term $\frac{p_{\text{inert gas}}}{p_{P_2} + p_{O_2}}$ should be multiplied by a factor $D_{\text{inert gas}}$ which measures the rate of diffusion of the active centres through the particular inert gas in question.*

If the pressure limit with a spark for hydrogen-oxygen mixtures is that of Hinshelwood and Thompson, a similar relationship can be derived, namely,

$$p_{H_2} p_{O_2} \left(1 + \frac{p_{\text{inert gas}}}{p_{H_2} + p_{O_2}} \right) d^2 = k,$$

⁶ Kowalsky, *Z. physikal. Chem.*, **11B**, 56, 1931.

⁷ Melville and Ludlam, *Proc. Roy. Soc.*, **132A**, 108, 1931.

⁸ Dalton and Hinshelwood, *Proc. Roy. Soc.*, **125A**, 294, 1929.

⁹ Semënov, *Z. Physik*, **46**, 113, 1927.

* A slight error was introduced into the paper of Melville and Ludlam. In reality the term $\frac{p_{\text{inert gas}}}{p_{H_2} + p_{O_2}}$ should be divided by the factor D . This is sufficiently obvious as not to need further explanation, and will be corrected by Melville in a further paper on this subject shortly to be published.

or, employing the correction of Melville and Ludlam,

$$p_{H_2} p_{O_2} \left(1 + \frac{D^{-1} \cdot p_{\text{inert gas}}}{p_{H_2} + p_{O_2}} \right) d^2 = k.$$

The validity of this relation forms the subject of this paper.

Apparatus and Procedure.

The gases or vapours to be investigated were respectively mixed with oxygen in the required proportions in a large storage vessel. Hydrogen, oxygen, carbon dioxide, helium, argon, nitrogen and nitrous oxide were taken from cylinders and dried by phosphorus pentoxide; sulphur dioxide was from the liquid. Chloroform, carbon tetrachloride and acetone, and the other compounds used were from redistilled specimens. The explosion vessel was a long cylindrical tube at the upper end of which was fitted a ground joint carrying the platinum electrodes. This joint was so constructed as to fit into tubes of different diameter, thus maintaining the same spark-gap in each case. The spark was produced by an induction coil using 6 volts in the primary circuit. The spark under these circumstances was not entirely reproducible, but as results showed was sufficiently so for the purpose involved, which was not so much to determine the absolute value of the limit as the variation of this with different factors. Explosion could usually be observed by the progress of the flame or by condensation of steam on the vessel walls. The movement of a mercury manometer column served as a check.

It was generally found that either explosion occurred immediately on making contact or not at all. When the mixture failed to explode, a slow combination of the gases around the spark naturally ensued. The limiting pressure for explosion could usually be determined to within 1 mm.

Results.

1. The Influence of Percentage Composition upon the Total Critical Pressure.

The change in the total critical pressure limit with change in percentage composition of the hydrogen-oxygen mixture was first examined in a vessel 3.3 cm. in diameter. Two series of experiments are given in Table I., and the curves of Fig. 1 show the variation of the total critical

TABLE I.

SERIES A.				SERIES B.			
Per Cent. H_2 .	$p_{\text{tot.}}$ mm.	p_{H_2} mm.	p_{O_2} mm.	Per Cent. H_2 .	$p_{\text{tot.}}$ mm.	p_{H_2} mm.	p_{O_2} mm.
27.5	22	6.1	15.9	22.1	21	4.6	15.4
41	24	9.8	14.2	37.9	22	8.4	15.6
52.8	24	12.7	11.3	47.4	20	9.5	10.5
53.8	23	12.4	10.6	58.8	29	17	12
66.5	36.5	24.9	11.6	65.5	34	22.2	11.8
66.8	36	24.1	11.9	79	47	37.2	9.8
78	59	46	13	80	51	41	10
83.5	60	50	10	87	76	66	10
86.5	100	86.5	13.5				
88	82	72	10				

pressure, and of the partial pressures of hydrogen and oxygen with percentage composition.

As this table shows, the critical partial pressure of oxygen over a wide range of composition does not vary greatly, but the hydrogen partial pressure varies considerably.

Validity of the Semënov relationship already discussed would imply constancy of the product $p_{H_2}p_{O_2}$ for the same vessel in the absence of inert gas; and the plot of p_{H_2} against p_{O_2} should be a rectangular hyperbola. Dalton and Hinshelwood found a discrepancy in this connection in the oxidation of phosphine.⁸ As later experiments prove, the "inert gas effect" of the hydrogen and oxygen themselves are such that it is not reasonable to expect a constancy of the product $p_{H_2}p_{O_2}$. The observations of Dalton and Hinshelwood are also probably to be explained in this way.

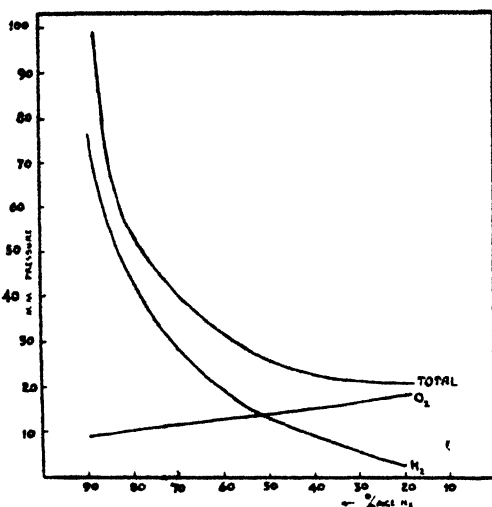


FIG. 1.

2. The Influence of Inert Gases.

The curves of Fig. 2 show how the presence of nitrogen in increasing proportion affects the total critical pressure for various hydrogen-oxygen ratios. The following summarises the data for the $2H_2:O_2$ ratio. It will be seen that under these circumstances addition of nitrogen appears to leave the total critical pressure (including the nitrogen) unaffected, until a rather high percentage of nitrogen is reached. This result was at first thought to be important, but a comparison with other similar inert gases will show that it is entirely fortuitous.

It is clear that

TABLE II.

Per Cent. N_2	P_{tot}	$P(2H_2 + O_2)$	P_{H_2}
0	37	37	0
21.3	37	29.1	7.9
38.9	37	22.6	14.4
53.3	37	17.3	19.7
64.5	39	13.8	25.2
74.2	43	11.1	31.9

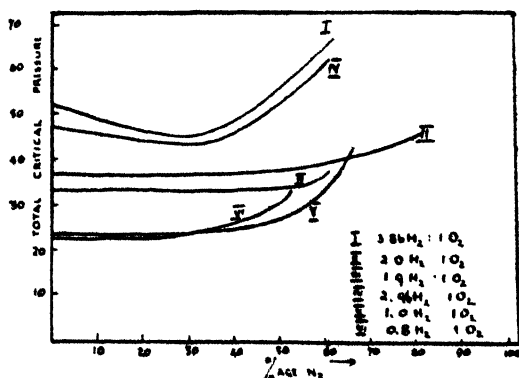


FIG. 2.

addition of nitrogen depresses the partial pressure of hydrogen plus oxygen required for explosion. This is demonstrated by Table II.

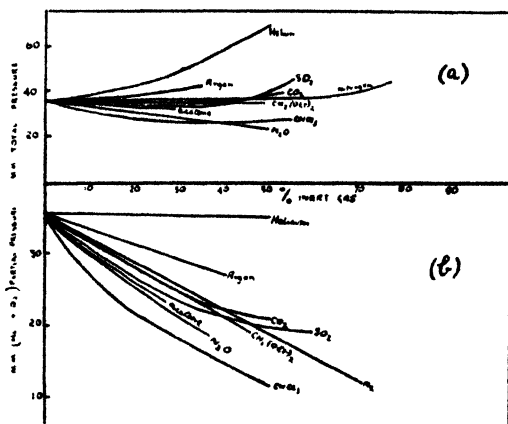


FIG. 3.

There is then no reason why hydrogen and oxygen themselves should not exert an inert-gas effect similar to that of nitrogen. Accordingly in order to make a comparison of the effect of nitrogen with that of other substances easier, it will be convenient always to use hydrogen and oxygen in the proportions 2 : 1. The inert-gas effect under these circumstances may be a minimum.

Fig. 3 shows the

effect of carbon dioxide, sulphur dioxide, nitrous oxide, argon, helium, acetone, formaldehyde ethylal, chloroform, and carbon tetrachloride upon the pressure limit. Curves (a) show the variation of total pressure, curves (b) that of the partial pressure of hydrogen plus oxygen.

Fig. 4 shows the plot of $\frac{1}{P_{H_2}P_{O_2}}$ against $\left(1 + \frac{P_{\text{inert gas}}}{P_{H_2} + P_{O_2}}\right)$ the results

being taken from Table III. Satisfactory straight lines are obtained. These break down, however, at higher concentrations of the inert gases, where the percentage of the reacting gases is small.

In the case of acetone only readings at comparatively low percentages of acetone will be legitimate. There seems in general to be a tendency for the lines to become steeper as the percentage of inert-gas increases. This may be the result of the inert-gas effect of the oxygen and hydrogen themselves, but it will be a matter for more detailed investigation. The inert-gas effects of the hydrogen and oxygen given in Table III. are estimated from Fig. 1.

The slopes of the lines of Fig. 4 follow the same order as was found by Melville and Ludlam.⁷ They do not appear to be sufficiently accurate, however,

to warrant a calculation such as was made by these observers to find the particular active product, the diffusion of which through the respective inert-gas would lead to the effect measured. For this reason they are being more carefully examined.

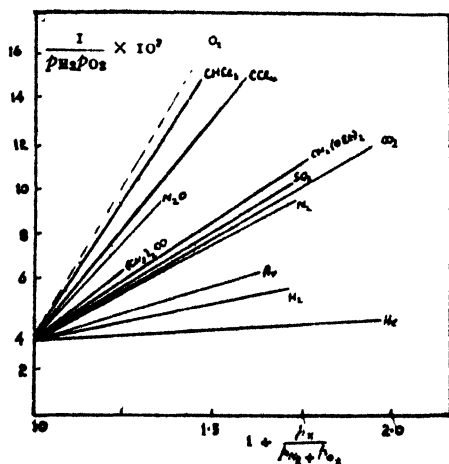


FIG. 4.

TABLE III.

x = inert gas.
 p_{tot} = total critical pressure.
 p_1 = partial pressure of hydrogen in mm.
 p_2 = " " oxygen " "
 p_3 = " " inert gas " "

% x .	$p_{\text{tot.}}$	p_1 .	p_2 .	p_3 .	$\frac{1}{p_1 p_2} \times 10^3$.	$\left(1 + \frac{p_3}{p_1 + p_2}\right)$.	% x .	$p_{\text{tot.}}$	p_1 .	p_2 .	p_3 .	$\frac{1}{p_1 p_2} \times 10^3$.	$\left(1 + \frac{p_3}{p_1 + p_2}\right)$.
x = Carbon Dioxide.							x = Nitrogen.						
0	36	24	12	0	3.47	1.0	0	37	24.5	12.5	0	3.27	1.0
12	35	20.5	10.3	4.2	4.74	1.14	21.3	37	19.3	9.8	7.9	5.29	1.27
21.5	35	18.4	9.1	7.5	5.97	1.27	38.9	37	15.0	7.6	14.4	8.77	1.64
30	35	16.3	8.2	10.5	7.46	1.42	53.3	37	11.5	5.8	19.7	14.99	2.14
40.3	37	14.8	7.3	14.9	9.26	1.67	64.5	39	9.2	4.6	25.2	23.64	2.82
51.1	42	13.7	6.8	21.5	10.73	2.05	74.2	43	7.4	3.7	31.9	36.5	3.88
x = Sulphur Dioxide.							x = Argon.						
0	36	24	12	0	3.47	1.0	0	36	24	12	0	3.47	1.0
10.1	34.5	20.7	10.3	3.5	4.65	1.13	3.5	36.5	23.5	11.7	1.3	3.64	1.04
22.2	33.5	17.4	8.7	7.4	6.6	1.28	7.0	37.5	23.3	11.6	2.6	3.74	1.07
30.5	34	15.7	7.9	10.4	8.06	1.44	15.5	39	22	11.0	6.0	4.13	1.26
42	37	14.3	7.2	15.5	9.7	1.72	24.1	41	20.7	10.3	10.0	4.7	1.32
54	50	15.3	7.7	22	8.47	1.95	35.8	43	18.4	9.2	15.4	5.92	1.56
x = Helium.							x = Nitrous Oxide.						
0	36	24	12	0	3.47	1.0	0	35.5	23.7	11.8	0	3.57	1.0
10	41	24.6	12.3	4.1	3.31	1.11	8.1	33.5	20.5	10.3	2.7	3.89	1.087
18.2	44.5	24.3	12.1	8.1	3.4	1.22	16.5	31.5	17.5	8.8	5.2	6.49	1.19
35	55	23.85	11.9	19.25	3.52	1.54	25	29	14.5	7.2	7.2	9.52	1.33
50	68	22.7	11.3	34.0	4.08	2.0	35.6	25.5	11.0	5.4	9.1	16.84	1.55
							47	23	8.2	4.0	10.8	30.5	1.88
							60	21.5	5.7	2.9	12.9	60.6	2.5
							75	31	5.2	2.6	23.2	74.1	3.97
x = Formaldehyde Ethylal.							x = Acetone.						
0	36	24	12	0	3.47	1.0	0	36	24	12	0	3.47	1.0
18	36	19.7	9.8	6.5	5.18	1.22	8.1	34.5	21.1	10.6	2.8	4.46	1.1
25.3	35	17.4	8.7	8.9	6.6	1.34	26.3	31	15.2	7.6	8.15	8.62	1.36
50	35	11.7	5.8	17.5	14.75	2.0	38.1	34	14.0	7.0	12.9	10.1	1.61
70	33	6.6	3.3	23.1	45.9	3.34							
x = Chloroform.							x = Carbon Tetrachloride.						
0	36	24	12	0	3.47	1.0	0	36	24	12	0	3.47	1.0
2.85	33.5	21.7	10.85	0.95	4.25	1.03	3.76	34	21.8	10.9	1.3	4.20	1.04
7.55	31.5	19.4	9.7	2.4	5.32	1.08	17.6	30	16.5	8.2	5.3	7.41	1.21
11.2	30	17.6	8.9	3.4	6.39	1.13	34	28.5	12.5	6.3	9.7	12.7	1.5
22.2	27	14	7.0	6.0	10.2	1.29	49.2	27	8.9	4.5	13.6	25.0	2.0
53.5	26	8.1	4.0	13.9	30.9	2.15							
x = Hydrogen.							x = Oxygen.						
66.7	36	24	12	0	3.47	1.0	33.3	36	24	12	0	3.47	1.0
70	39	23.4	11.7	3.9	3.65	1.11	40	30	18	9	3	6.17	1.11
75	45	22.4	11.2	11.4	4.0	1.34	45	27	14.8	7.2	5	9.43	1.23
80	52	20.8	10.4	20.8	4.63	1.67	50	25	12.5	6.2	6.3	12.9	1.34
85	65	19.5	9.75	35.75	5.29	2.22	60	23	9.2	4.6	9.2	23.6	1.66

The general outline of the fact is, meanwhile, such, that there can be no doubt but that diffusion of the active product to the walls is most important in determining the propagation of the chains.

3. The Influence of the Vessel Dimensions.

The influence of the vessel dimensions can conveniently be estimated by comparing the critical explosion pressure of various hydrogen-oxygen mixtures in two vessels of different diameter. Two tubes of 3.3 cm. and 5.0 cm. diameter were used. The critical pressure is in general lower in the wider vessel than in the narrower one. Considering the $2\text{H}_2 : \text{O}_2$ mixtures and neglecting the inert-gas effects of the hydrogen and oxygen themselves, we shall expect the relationship

$$p_{\text{H}_2} p_{\text{O}_2} \cdot d^2 = k$$

to hold approximately. As Table IV. shows, this appears to be true, though the calculated power of the vessel diameter would be 2.1 rather than 2.

TABLE IV.

Vessel Diameter cm.	$p_{\text{tot.}}$	p_{H_2}	p_{O_2}	$p_{\text{H}_2} p_{\text{O}_2} \cdot d^2$
3.3	36	24	12	3140
5.0	22	14.7	7.3	2690

The influence of inert-gases also leads to another method of estimating the effect of vessel size. The influence of nitrogen, sulphur dioxide, and chloroform was examined in the wider vessel, with the results shown in Table V.

TABLE V.

Per Cent. x_2	$p_{\text{tot.}}$	p_{H_2}	p_{O_2}	p_{x_1}
$x = \text{Sulphur Dioxide.}$				
0	23	15.2	7.7	0
10	21.5	12.9	6.45	2.15
16.6	21.5	11.9	6.0	3.6
22	21.5	11.18	5.59	4.73
28	22	10.5	5.3	6.2
48.5	33	11.3	5.7	16
$x = \text{Chloroform.}$				
0	22.5	15	7.5	0
10	20.5	12.3	6.2	2.0
15.5	20	11.3	5.6	3.1
23	19	9.7	4.9	4.4
33	18.5	8.3	4.1	6.1
$x = \text{Nitrogen.}$				
0	23	15.3	7.7	0
8.0	23	14.1	7.1	1.8
15	23.5	13.3	6.7	3.5
26	24	11.9	5.9	6.2
35	25.5	11.1	5.5	8.9
63	37	8.7	4.3	24

When plotted as $\frac{1}{p_{H_2}p_{O_2}}$ against $\left(1 + \frac{p_{\text{inert-gas}}}{p_{H_2} + p_{O_2}}\right)$ these data give satisfactory straight lines. Comparing the slopes of these lines with those previously obtained in the narrower vessel, we should, if the Seménov equation holds, expect them to be in the ratio $5^2:3.3^2$. This is approximately, though not exactly so. It is likely that the inexact agreement is due to inert-gas effects of the hydrogen and oxygen themselves, or simply irregularities in the observations.

4. The Effect of Temperature.

All the experiments described above were carried out at room temperature. It is hoped from further investigations at higher temperature to obtain information about the nature of the chains.

TABLE VI.

Vessel Diameter.	Slopes.		
	Chloroform	Sulphur Dioxide.	Nitrogen.
5.0	22	10	9
3.3	42	22	17
Ratios: $(1.52)^2 = 2.3$	1.9	2.2	1.9

5. Discussion.

It seems that the above results are really to be interpreted in the way already outlined, namely that the propagation of chains depends upon the latter not reaching the vessel walls. Inert-gases effect a continued propagation and more successfully in the order of decreasing diffusion coefficients.

At the same time another property of these inert-gases—their thermal conductivity—might play a part. How far this is important, if at all, will be discussed in later work.

Referring back to Fig. 4 it is seen that oxygen is apparently especially favourable as inert-gas for the propagation of chains. We should, *a priori*, have expected to find oxygen about as effective as nitrogen in this respect. Probably the increased effectiveness is due to some specific action of oxygen in the chain; reaction chains are as a rule very much favoured by increased oxygen pressure. Information of this kind may help in elucidating the nature of the hydrogen-oxygen chain.

Whilst all the foregoing arguments are valid, it is really by no means proved that the limit of pressure here involved is the same as that investigated by Thompson and Hinshelwood, as Haber and others would suggest. If this were so, it would be necessary to remember in discussing, the facts here given that in the case of the spark experiments at least, the active centres originated in the gas. One result at any rate leads us to suppose that critical limits with a spark are more common than might be expected. It has now been found that methane-oxygen mixtures cease to explode with a spark if the pressure falls below a certain limit. This phenomenon has been investigated along entirely

similar lines to the above, and the results will shortly appear elsewhere. The facts are essentially identical with those described here. It may be possible, confining one's attention to the effect of one inert gas such as nitrogen, to compare the diffusion coefficients of the respective active centres in the hydrogen-oxygen reaction on the one hand and the methane-oxygen on the other. This might lead with certain approximations to a knowledge of the relative masses of the active products. Assuming that hydrogen atoms or hydroxyl radicals are the active centres in the former case, it may be possible to estimate whether the idea of a peroxide body $\text{CH}_4 : \text{O}_2$ would satisfy the necessary requirements in the combustion of methane.

My thanks are due to Dr. B. Lambert, for the loan of a high-speed pump which was of great service in this work.

*St John's College and The Old Chemistry Dept.,
University Museum, Oxford.*

THE OXIDATION OF PHOSPHORUS VAPOUR AT LOW PRESSURES.

BY H. W. MELVILLE.

Received 18th January, 1932.

Within the past few years a number¹ of chemical reactions have been studied which possess a rather peculiar characteristic. The addition of an inert gas to the reaction mixture results in an increase in the reaction velocity. Reactions which exhibit this behaviour are chain reactions. According to the theory of chain reactions this increase is explained by supposing that the chains are terminated when they encounter the wall of the reaction vessel. The presence of an inert gas, by decreasing the mean free path of the molecules in the reaction mixture prevents the chains from reaching the walls and thus enables the chain to be longer than it normally would have been; this results in an increase of the reaction velocity.

In chain reactions which proceed explosively, for example, the oxidation of phosphorus² and phosphine³ at low pressures, the effect of inert gases is to accelerate the reaction velocity but the effect is made evident by the inert gas lowering the *lower* critical oxidation pressure. That is, the inert gas facilitates the occurrence of explosion.

The effect of the inert gas can be expressed quantitatively by an equation originally deduced by Semenoff.² If p_{P_4} , p_{O_2} , p_x , are the pressures of phosphorus, oxygen and inert gas respectively then, at the lower explosion limit,

$$p_{\text{P}_4} \cdot p_{\text{O}_2} \left(1 + \frac{p_x}{p_{\text{P}_4} + p_{\text{O}_2}} \right) = \text{constant} . \quad . \quad . \quad (1)$$

¹ For example the $\text{H}_2\text{-O}_2$ reaction, Gibson and Hinshelwood, *Proc. Roy. Soc.*, **119A**, 591, 1928.

² Semenoff, *Z. Physik*, **46**, 109, 1927; *Z. physikal. Chem.*, **2B**, 161, 1929.

³ Dalton and Hinshelwood, *Proc. Roy. Soc.*, **125A**, 295, 1929.

provided the explosions are confined to a vessel of a given size. Now (1) indicates that the inert gas effect should be independent of the nature of the gas. This result is due to the assumption that the molecules P_4 , O_2 and X have the same mass and diameter and that therefore the mean free path is inversely proportional to the total pressure.

Subsequent work⁴ on this effect has shown that (1) does not describe exactly the effect of gases on the lower critical oxidation limit of phosphorus. From (1) it is seen that if $1/p_{O_2}$ is plotted against

$1 + \frac{p_x}{p_{P_4} + p_{O_2}}$ a straight line should be obtained. The slope A of this line is, however, dependent on the nature of X . It was found that when the diffusion coefficient D of oxygen molecule through X is multiplied by A an approximately constant quantity was obtained.

Recently H. W. Thompson⁵ has found that a similar relationship holds for the lower critical oxidation limit of hydrogen. The effect also extends to the oxidation of methane. Equation (1) is thus modified (empirically) to

$$p_{P_4} \cdot p_{O_2} \left(1 + \frac{D^{-1} p_x}{p_{P_4} + p_{O_2}} \right) = \text{constant}^* \quad (2)$$

In order to deduce this equation the original theory must be modified to some extent. The problem is very complicated since the rate of diffusion of a reaction chain involves the diffusion of the two propagators into a ternary mixture. Semenoff⁶ has attempted an exact solution of the case for the hydrogen-oxygen reaction assuming the propagators were H and excited HO_2 molecules. This treatment is not suitable for the above case. Another attempt at an exact kinetic theory analysis of the diffusion of reaction chains was made recently by Bursian and Sorokin,⁷ but their treatment is not applicable in the present case since these investigators assumed at the outset that the masses and diameters of the reacting molecules were equal.

The following consideration represents an attempt to obtain (2) on as simple a basis as possible. Following Dalton and Hinshelwood⁸ let the chain propagators be X_O and X_P and assume that X_O is produced spontaneously at a rate $k_1 F(c)$ in the reaction mixture, that X_O collides with P_4 to give X_P and that X_P collides with O_2 to give X_O then for the stationary state.

$$\frac{dp_{X_O}}{dt} = k_1 F(c) + \alpha k_2 p_{X_P} p_{O_2} - k_3 p_{X_O} p_{P_4} - K p_{X_O} = 0, \quad (3)$$

$$\frac{dp_{X_P}}{dt} = k_3 p_{X_O} p_{P_4} - k_2 p_{X_P} p_{O_2} - K p_{X_P} = 0 \quad (4)$$

α introduces the branching chain hypothesis. K is the rate at which X_O and X_P reach the wall of the vessel and are destroyed. For the condition of explosion, i.e., $p_{X_O} = \infty$

$$(\alpha - 1) k_3 p_{P_4} p_{O_2} = K(p_{O_2} + p_{P_4}) \quad (5)$$

⁴ Melville and Ludlam, *Proc. Roy. Soc.*, **132A**, 108, 1931.

⁵ See page 299.

⁶ A misprint occurs in ref. 4 on p. 125. The letter D should be written D^{-1} .

⁷ *Z. physikal. Chem.*, **2B**, 169, 1929.

⁸ *Ibid.*, **12B**, 247, 1931.

According to the Einstein-Smoluchowski diffusion law the time (t) required for a molecule to reach a point distant x from the original position is connected with the diffusion coefficient of the molecule through the gas by the equation

$$x^2 = 2Dt \quad . \quad . \quad . \quad . \quad . \quad (6)$$

K is inversely proportional to t and D is inversely proportional to the total gas pressure (equal masses and diameters), and if x is the radius of a cylindrical reaction vessel then $K \sim \{x^2(p_{P_4} + p_{O_2} + p_x)\}^{-1}$ so that substituting in (5), (1) is obtained.

Consider now a single molecule diffusing through a ternary gas mixture in which the diffusion coefficients for each gas separately are D_1 , D_2 and D_3 . If t is the time required to diffuse a given distance then assume that

$$t \sim \frac{1}{D_1} + \frac{1}{D_2} + \frac{1}{D_3} \quad . \quad . \quad . \quad . \quad . \quad (7)$$

For a single gas $D \sim \frac{1}{M^{\frac{1}{2}} p \sigma^2}$ where M is the molecular weight, p the pressure, σ the molecular radius. Therefore

$$\begin{aligned} K &\sim \frac{1}{1/D_1 + 1/D_2 + 1/D_3} \\ &\sim (M_1^{\frac{1}{2}} p_1 \sigma_1^2 + M_2^{\frac{1}{2}} p_2 \sigma_2^2 + M_3^{\frac{1}{2}} p_3 \sigma_3^2)^{-1} \quad . \quad . \quad . \quad (8) \end{aligned}$$

Let $\sigma_1 = \sigma_2$ and $M_1 = M_3$ these being constants of any particular reaction then multiplying (8) by $\sigma_1^2 M_1^{\frac{1}{2}}$

$$K \sim \left(p_1 + p_2 + \frac{\sigma_3^2 M_3^{\frac{1}{2}}}{\sigma_1^2 M_1^{\frac{1}{2}}} \cdot p_3 \right)^{-1} \quad . \quad . \quad . \quad (9)$$

From (5) and (9)

$$p_{P_4} \cdot p_{O_2} \left(1 + \frac{\sigma_3^2 M_3^{\frac{1}{2}}}{\sigma_1^2 M_1^{\frac{1}{2}}} \cdot \frac{p_x}{p_{P_4} + p_{O_2}} \right) = \text{constant} \quad . \quad (10)$$

The variable which determines the magnitude of the effect of X is thus $\sigma_3^2 M_3^{\frac{1}{2}}$. Let $\sigma_1^2 M_1^{\frac{1}{2}} = k$ and substituting for $\sigma_3^2 M_3^{\frac{1}{2}}$ the more complicated factor $\sigma_{AX}^2 \left(\frac{1}{M_A} + \frac{1}{M_X} \right)^{-\frac{1}{2}}$ as demanded by the Stefan-Maxwell theory for the diffusion of a binary mixture (10) becomes

$$p_{P_4} \cdot p_{O_2} \left(1 + \frac{\sigma_{AX}^2 (1/M_A + 1/M_X)^{-\frac{1}{2}}}{k} \cdot \frac{p_x}{p_{P_4} + p_{O_2}} \right) = \text{constant} \quad (11)$$

where M_A and M_X are the molecular weights of the diffusing molecule and of X . σ_{AX} is the sum of the radii of A and X . M_A and σ_A will be mean values since they represent the effect of X_O and X_P .

It emerges, therefore, that the factor multiplying p_x is not the diffusion coefficient (it is only inversely proportional to it) but a factor expressing the molecular weight and effective collision diameter of the inert gas molecules. For some particular gas this factor will be equal to unity. In the phosphorus experiments it would appear that the more complicated organic molecules fulfil this condition. Thus (10) will assume the simpler form (1). For simpler molecules the factor is less than unity.

Inhibition in the Gas Phase.

If, in addition, the added gas X is able to stop the reaction chains in the gas phase the equations developed above must be modified. This correction has been developed from a theory of Kowalski,⁸ and it has been shown⁴ that

$$k'A = 1 - 1/a e^{-U/RT} \quad . \quad . \quad . \quad (12)$$

where k' and a are constants and $e^{-U/RT}$ is the ratio of the number of collisions stopping the chains to the total number of collisions of X with the reaction chains. There is reason to believe⁹ that a is not less than 0.1 and may possibly be equal to unity. In the latter case (12) may be written

$$k'A = 1 - e^{-U/RT} \quad . \quad . \quad . \quad (13)$$

and hence if $e^{-U/RT} = 1$, $A = 0$. If A has a value less than that expected from the diffusion coefficient for X this deviation may be ascribed to the termination of reaction chains in the gas phase. This result also follows from equations (3) and (4) of Dalton and Hinshelwood, (3) being modified to

$$\frac{dp_{X_0}}{dt} = k_1 F(c) + \alpha k_2 p_{X_0} p_{O_2} - k_3 p_{X_0} p_{P_4} - k_4 p_{X_0} p_X - K p_{X_0} = 0 \quad (3')$$

the penultimate term representing the inhibitory effect of X. If $k_4 = k_3 = k_2$, (5) becomes

$$(\alpha - 1)k_3 p_{P_4} p_{O_2} = K(p_{P_4} + p_{O_2} + p_X) \quad . \quad . \quad (5')$$

or substituting the value of K

$$p_{P_4} \cdot p_{O_2} = \text{constant},$$

so that the lower critical oxidation limit is unaffected by the addition of X. The inhibitory effect thus balances the diffusion effect.

This inhibition may explain the relatively small influence of acetone and formaldehyde ethylal in Thompson's H_2/O_2 experiments. A well-defined inhibitory action has been found for the $P_4 - O_2$ reaction at low pressures, tetraethyl lead being used.

If tetraethyl lead acts as an inert gas its effect should be approximately equal to that of mesitylene or methylene chloride, $A = 1.30$ whereas from the results given in Table I., $A = 0.74$. From equation (13) $e^{-U/RT} = 0.4$, i.e. 1 collision in every 2.5 is effective in terminating the chain. For comparison the results for methylene chloride are given. D for tetraethyl lead cannot be calculated since the molecular diameter has not yet been measured. An estimate of this magnitude may be made from the parachor and D finally calculated giving a value close to that for mesitylene.

Pressures are in mm. Hg. The two series of experiments were carried out under slightly different conditions, which accounts for the small difference in p_{O_2} , for $p_X = 0$.

Equation (13) also explains another peculiarity of the oxidation of phosphorus at low pressures. On Semenov's theory atomic oxygen is one of the chain propagators. From the experiments of Harteck

⁸ *Z. physikal. Chem.*, **4B**, 288, 1929.

⁹ *Ibid.*, **2B**, 161, 1929.

and Kopsch¹⁰ on the reactions of atomic oxygen with organic compounds (vapours) and other gases it would be expected that most organic compounds would act as inhibitors for the $P_4 - O_2$ reaction since these compounds are completely oxidised under the experimental conditions of Hardeck and Kopsch. As is seen from (13), however, $e^{-U/RT}$ must be at least 0.1 or 1 in 10 collisions must be effective if inhibition is to be noted since the experimental error is of the order of 10 per cent. In the reaction tube employed by Hardeck and Kopsch an oxygen atom could make as many as 10^8 collisions with other gas molecules present so that even if oxidation only occurred with a collision efficiency of 10^{-6} it would be readily detectable. The atomic oxygen technique is thus

TABLE I.

Methylene Chloride.				Tetraethyl Lead.			
p_X	p_{O_2}	$1/p_{O_2}$	$\frac{p_X}{1 + p_{P_4} + p_{O_2}}$	p_X	p_{O_2}	$1/p_{O_2}$	$\frac{p_X}{1 + p_{P_4} + p_{O_2}}$
0	0.068	14.7	1.00	0	0.054	18.5	1.00
0.027	0.055	18.2	1.45	0.032	0.041	24	1.67
0.054	0.041	24	1.82	0.035	0.041	24	1.73
0.070	0.032	31	2.2	0.054	0.036	28	2.25
0.081	0.034	29	2.4	0.059	0.035	29	2.40
0.089	0.026	38	2.7	0.068	0.029	35	2.90
0.097	0.029	34	2.8	0.076	0.033	31	2.93
0.119	0.019	53	3.7	0.078	0.026	38	3.36
0.135	0.017	59	4.2	0.084	0.026	38	3.50
0.162	0.014	71	5.2	0.095	0.023	43	4.16
0.170	0.013	77	5.5	0.108	0.022	46	4.80
0.197	0.011	91	6.5	0.122	0.019	53	5.70
0.216	0.009	110	7.4	0.122	0.018	56	5.98
0.219	0.008	120	7.6	0.138	0.013	80	8.1

much more sensitive than the low pressure explosions of $P_4 - O_2$ mixtures as a detector of oxidation by atomic oxygen. This explains the discrepancy between the two series of experiments.

At the upper critical explosion limit of phosphorus vapour termination of the chains takes place entirely in the gas phase. In the following treatment an attempt is made to calculate the efficiency of the deactivating process. It will be assumed (1) the influence of the size of the reaction tube is negligible; (2) X_0 is destroyed by collision with O_2 and (3) with X . Equations (3) and (4) are therefore written

$$\frac{dp_{X_0}}{dt} = k_1 F(c) + \alpha k_2 p_X p_{O_2} - k_3 p_{X_0} p_{P_4} - k_4 p_{X_0} p_{O_2} - k_5 p_{X_0} p_X = 0 \quad (14)$$

$$\frac{dp_{X_P}}{dt} = k_2 p_{X_0} p_{P_4} - k_2 p_X p_{O_2} = 0 \quad (15)$$

Solving for p_{X_P} , then p_{X_0} and introducing the condition for explosion

$$k_3 p_{P_4} (\alpha - 1) = k_4 p_{O_2} + k_5 p_X \quad (16)$$

¹⁰ *Z. Electrochem.*, **36**, 714, 1930; *Z. physikal. Chem.*, **12B**, 327, 1931.

p_{0_2} being the upper critical explosion pressure. There are experimental data in support of (15) from the experiments of a number of authors. If $p_X = 0$, then $p_{0_2} \sim p_{P_4}$ which has been found to be the case by Kowalski.⁸ If p_{0_2} is kept constant p_X will increase with p_{P_4} , (Emeleus¹¹). The presence of X reduces p_{0_2} —an effect which has been known for many years. To enquire into this question more closely (16) may be rearranged

$$p_{0_2} = \frac{k_3/k_5 p_{P_4} (\alpha - 1)}{k_4/k_5 + p_X/p_{0_2}} = \frac{k}{a' + p_X/p_{0_2}} \quad (17)$$

This equation has been found by Schacherl¹² to express the behaviour of nitrogen peroxide with a considerable degree of accuracy. A number of other substances also conform to this equation.¹³ For a given substance k and a' are characteristic the reciprocals of k and of a' being a measure of the efficiency of X as a poison since they contain the constant k_5 . The ratio k/a' according to (17) should be independent of X. These relationships are shown in table II., the data being obtained from Tausz and Gorlacher's experiments.

TABLE II.

Gas.	a' .	K.	a'/K .	Efficiency of Inhibition Collisions.
Sulphur Dioxide . . .	23	13520	390	6×10^{-6}
Benzene	21	10800	510	8×10^{-6}
Cyclohexane	20	10100	500	9×10^{-6}
Acetylene	11.3	7020	350	1.2×10^{-4}
Methylcyclohexane .	8.2	4530	550	1.8×10^{-4}
Ethylene	1.75	1070	610	7×10^{-4}
Propylene	0.35	168	480	5×10^{-2}
Cyclohexene	0.11	58	530	1.4×10^{-2}
Isoprene	0.025	20	800	4×10^{-2}
Iron Pentacarbonyl .	0.0033	1.7	520	5×10^{-1}

The common gases, *e.g.* N_2 , CO_2 , H_2 , etc., have only a small effect on the upper critical limit and the results of different investigators are not in very good agreement. If it is assumed that iron penta-carbonyl is as efficient a poison as tetraethyl lead then from the value of K the absolute values of the efficiency of the poison may be calculated. This is given in the last column of the above table. It is of importance to note that the efficiencies lie between 10^{-1} and 10^{-6} in agreement with the experiments of Harteck and Kopsch.

Effect of Ozone and of Phosphine at Low Pressures.

The effect of ozone and of phosphine on the behaviour of $P_4 - O_2$ mixtures has also been investigated at low pressures, both gases giving abnormal results. Kowalski had found⁸ that ozone raises the upper critical explosion limit, that is, it facilitates the propagation of the reaction chains. Corresponding to this, at low pressures ozone reduces

¹¹ *J. Chem. Soc.*, 1336, 1926.

¹² *Coll. Czech. Chem. Comm.*, 2, 665, 1930.

¹³ Centnerszever, *Z. physikal. Chem.*, 26, 9, 1898; Tausz and Gorlacher, *Z. anorg. Chem.*, 190, 95, 1930.

the critical explosion pressure. For instance, with less than 5 per cent. ozone in the oxygen the pressure of the mixture for explosion was about 20 per cent. less than that without ozone. It is evident therefore, that ozone decreases the explosion pressure in some way which is different from the normal diffusion effect since this would amount to a decrease of 1 to 2 per cent.

Phosphine has an exactly opposite effect—it *raises* the lower critical pressure of $P_4 - O_2$ mixtures. This effect is entirely unexpected from the theoretical point of view, for if PH_3 is a strong inhibitor *in the gas phase* it should have little or no influence. This seems to indicate that the effect is connected with the initiation of the chains. But theory shows that the explosion limit is not affected by the rate of production of the centres which start the chains providing, of course, that a finite number of centres is produced. It may be that phosphine can reduce this number to such a small value that the explosion limit is affected. While it has not yet been proved whether the chains in this particular

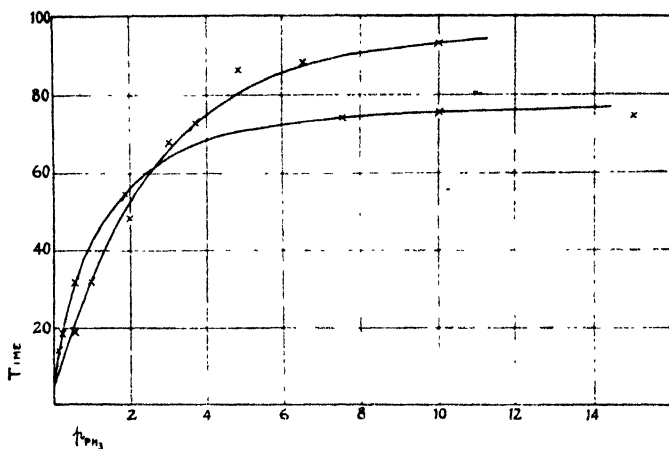


FIG. 1.

reaction are initiated in the gas phase or at an interface, it would appear that an interface is more suitable than the gas phase for inhibition to exert its full influence.

On the other hand if the chains can make elastic collisions with the walls of the containing vessel it is probable that the condition of the wall may alter the explosion pressure. Experiments have been made with walls of various substances, "clean" glass, paraffin wax, platinum, but no significant variations were obtained. This was probably due to the walls being covered with oxides of phosphorus since several explosions must take place in any one tube in order to measure the critical pressure. Owing to an accident during the course of these experiments one of the reaction tubes was covered with a layer of concentrated sulphuric acid from an adjacent manometer. It was then found that in this tube the explosion pressure had fallen to about half its initial value. That is a sulphuric acid surface reflects the chains better than a glass surface covered with oxides. Correspondingly, phosphine may be adsorbed on the oxide coated wall yielding a surface which is much more effective in the termination of chains than the oxides alone. The critical explosion pressure is thus raised. In this connection it may be pointed

out that the curve obtained by plotting explosion pressure against phosphine pressure resembles an adsorption isotherm (Fig. 1). Another observation supports this view. After a series of experiments had been carried out with phosphine the tube had to be pumped out for an unduly long time before the explosion pressure fell to its original value. In

TABLE III.

Pressure of PH_3 .	Time* for Explosion. (Sec.)	Pressure of PH_3 .	Time for Explosion. (Sec.)
0.0	5.0	0.0	6.0
0.1	14.0	0.5	19.2
0.2	18.4	0.9	32.0
0.5	31.4	1.3	28.0
2.2	58	2.0	48.0
5.0	75	2.6	61
7.5	72.4	3.0	67
10.0	75	3.7	72
15.0	72	4.8	86
		6.5	87
		10.0	94

one experiment when pumping out normally required two minutes the process had to be carried on for thirty minutes to regain normal conditions.

If the effect is due to inhibition in one of the forms suggested above it is all the more surprising since phosphine itself is spontaneously inflammable in oxygen. Two series of experiments are recorded in Table III. to show the magnitude of the effect.

The addition of phosphorus vapour to phosphine *reduces* the lower critical explosion pressure of phosphine as is shown here.

Pressure of Phosphorus. (mm.)	Time for Explosion.
0	1 min. 40 secs.
0.007	1 " 22 "
0.025	0 " 51 "

These phenomena are being investigated in more detail in order to ascertain what light they may ultimately throw on the phenomena of the low pressure oxidation of phosphorus and of phosphine.

* This is the time required for oxygen to leak through a capillary into the reaction tube.

SECTION III.—THEORIES OF THE ADSORPTION OF GASES. A GENERAL SURVEY AND SOME ADDITIONAL REMARKS.

INTRODUCTORY PAPER TO SECTION III.

BY M. POLANYI.

Received 29th December, 1931.

The adsorption of gases is observed mostly on solid substances so in general we can limit ourselves to this case. However, that does not prevent us from occasionally mentioning the adsorption of gases on liquid surfaces, especially on mercury, and also incidentally bringing forward types of adsorption other than of gases.

Part I.—Forces of Adsorption.

During the last decade the idea has prevailed that the atomic forces are of an electrostatic nature. It is only recently that Heitler and London,¹ for the homopolar valence energy, S. C. Wang,² and F. London,³ for the cohesion energy, have brought forward the proof that these phenomena are chiefly caused by the fact that when two atoms or molecules are brought together deeper lying quantum states are formed. Our conception of the forces effective in adsorption has been correspondingly modified also. Nevertheless it is advisable to keep the purely electrical forces in mind, for their effect may often be very noticeable.

1. Electrostatic Forces.

The electrostatic field at the boundary of a solid substance is only considerable if the substance is built up of ions. As an example of this we can take a KCl crystal, the calculations for which have been carried out by Blüh and Stark⁴ as well as Lennard-Jones and Dent.⁵

Fig. 1 shows the potential energy of a univalent ion at a (100) plane of a KCl lattice as a function of the distance. At the distance $r/a = 0.6-0.7$, where one can consider an adsorbed particle to be in equilibrium, the energy amounts to 1000-3000 small calories per mole.

Such a high potential for an adsorbed molecule, which as a whole is electrically neutral, could, however, only be attained if the molecule were composed of ions completely separated electrically, so that by suitable orientation the potential energy of an elementary charge could attain its full value. In reality, however, in a heteropolar molecule the "effective charge" = $\frac{\text{electrostatic charge}}{\text{distance between nuclei}}$ is seldom larger than one-fifth of the elementary charge.

¹ *Z. Physik*, **44**, 455, 1927.

² *Physik. Z.*, **28**, 663, 1927.

³ *Z. Physik*, **63**, 245, 1930.

⁴ *Ibid.*, **43**, 575, 1927.

⁵ *Trans. Far. Soc.*, **26**, 92, 1928.

In order to estimate the potential which is attained by a heteropolar molecule in the field of a crystal, let us consider its electric moment μ to be localised in a point. It then results that the potential energy, field strength times moment ($F\mu$), for the example of a NaCl crystal is given by the product of the ordinate in Fig. 2 by μ . For molecules with a large dipole, for example SO_2 ,

$\mu = 1.8 \times 10^{-18}$,
for the distance
 $r/a = 0.6-0.7$

the potential is 500-1500 calories. For molecules with small dipoles, for example CO_2 ,

$$\mu = 0.2 \times 10^{-18}$$

the potential is only 200-600 calories.

The potential which the electrical field exerts on a neutral molecule with the polarisability α amounts to $\frac{F^2\alpha}{2}$. Even for molecules with high polarisability, e.g., CO_2 , $\alpha = 8 \times 10^{-24}$; this potential has for the region $r/a = 0.6-0.7$ only the quite unimportant value of 100-300 calories.

Now it may happen that the electrical field of the solid wall occasionally has an appreciably higher value than that on a rock-salt (100) plane (for example on the (111) plane of the same crystal). But as a practical upper limit of the field we may take that of a free ion at a molecular distance of about 4 Å. That is

$$\frac{4.8 \times 10^{-10}}{(4 \times 10^{-8})^2} = 0.3 \times 10^6$$

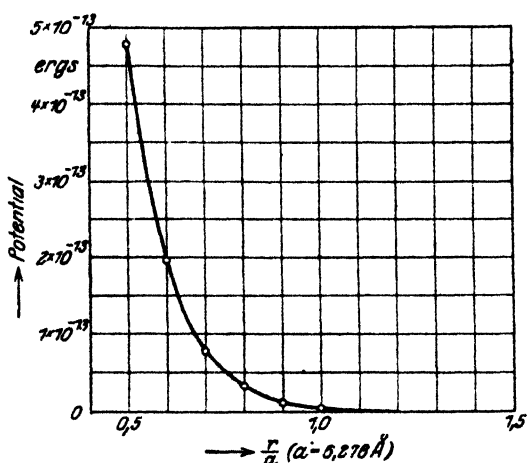


FIG. 1.—Potential energy of a monovalent ion at a (100) plane of KCl (according to Lennard-Jones and Dent).

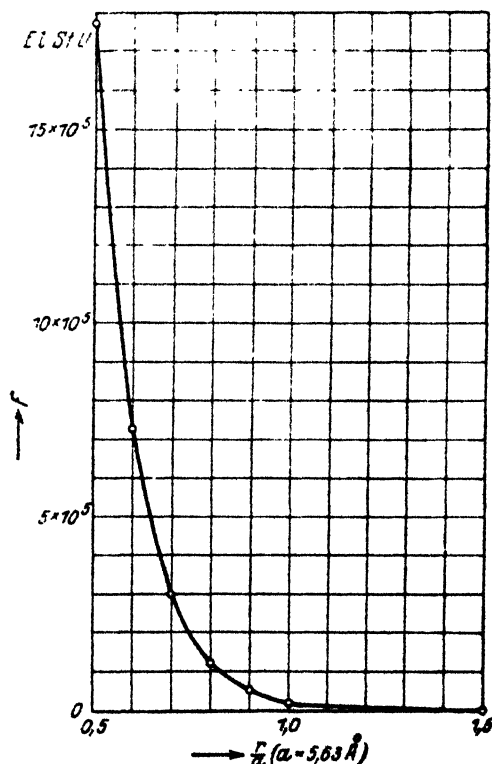


FIG. 2.—Force of electric field at a (100)-plane of NaCl (according to Lennard-Jones and Dent).

or ten times the value of the field of the (100) plane of rocksalt. However, on the surface of the usual adsorbents, charcoal, SiO_2 , etc., the electrical field is much smaller than in the case of NaCl because in these substances the charges are much less widely separated than in rocksalt.

In the case of adsorption on metals, the mirror forces come into play as a purely electrical agency. If one assumes the distance between the molecule and the mirror image to be 4 Å. then the energy $\left(\frac{\text{moment}^2}{\text{distance}^3}\right)$ for a strong dipole with $\mu = 2 \times 10^{-18}$ can amount to 3000 calories. For weak dipoles it would be vanishingly small. The experiments of H. Cassel⁶ in regard to the adsorption of H_2O on mercury show that the mirror forces are actually small.

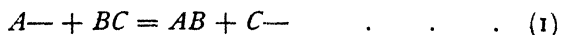
Thus, on the whole, the electrostatic adsorption field is only rarely so large that it can cause an appreciable part of the adsorption potential of several thousand calories which has been observed for the adsorption of substances such as CO_2 , SO_2 , $\text{C}_2\text{H}_5\text{Cl}$ on charcoal, silica gel, oxides, etc. An exception to this arises in the case when ions are present in the surface, for here they would act as quite strong electrical centres on molecules with a large dipole moment.

Molecules with a small dipole moment and electrically neutral substances should accordingly not be markedly adsorbed at all in an electrical way. In the following paragraphs we shall bring forward further facts which point in the same direction. (See Section on "Dispersion Forces.")

2. Valence Forces.

Of the various kinds of valence activity the best known one is that discovered by Heitler and London, *i.e.*, the binding forces between *S*-electrons. The theory of these forces describes the play of the homopolar valence forces in such a typical way that one is inclined to generalise their fundamental features. In the following we shall make such a generalisation by assuming the properties of the Heitler-London valence for the valence forces which are effective on the interface of a solid body.

Contrary to the assumption, which was formerly implicitly made in general, a free valence, according to the London theory, exerts no attraction on a molecule but rather a repulsion. This repulsion can be overcome if a strong collision or a force of another kind presses the two constituents close to one another. In this case a chemical change takes place through which generally a part of the reacting molecule is split off in the sense



Only when *BC* contains a double bond, or when a higher valence state is latent in it, can a union take place by the formation of a free radicle in the sense

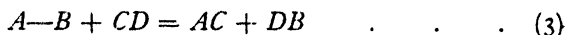


Thus, if the surface of a solid body contains an atom *A* —, out of which extends a free valence, this point of the surface exerts no attraction. A gas molecule can, however, after passing over a more or less high potential barrier, enter into a reaction with it, either decomposing according to (1), or forming with it according to (2) a complex which has a free valence, a "surface radical." The latter case can be con-

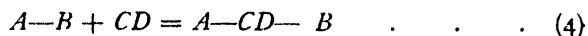
⁶ *Naturw.*, 19, 110, 1931.

sidered as an adsorption belonging to the type which is accompanied by a heat of activation.

Another possible kind of valence activity on a surface was pointed out on a former occasion⁷ and has recently been discussed in somewhat more detail.⁸ We refer to the effect of a *pair of valencies* loosely attached (symmetrically coupled) to one another.⁹ A pair of surface atoms *AB* bound by a loose valence bridge would easily react with a gas molecule *CD* splitting the latter up in the sense



or, if *CD* has a double bond, to give an addition



Both (3) and (4) are to be considered as adsorption processes in which the adsorbed gas is bound as a surface compound. The possibility of such surface compounds was first assumed by I. Langmuir, who has also given in the example of tungsten and oxygen the first proof of their existence.¹⁰ For a series of other cases, which probably have to be classified here, I refer to the contribution of A. F. Benton to the present discussion.

The formation of surface compounds must be generally accompanied by a heat of activation, which however can be very small.¹¹ It seems probable, that the heat of activation derived by H. S. Taylor¹² from the temperature coefficient of the rate of adsorption is of this kind.

The experiments on interference of electrons on surfaces¹³ indicate that the addition of adsorbed gases takes place frequently in the gaps between the atoms of the adsorbing surface and also leads to a loosening of the surface layer thus allowing a penetration into the inner part of the same.¹⁴ Hence it appears that the surface layer is able to absorb foreign substances to a greater extent than the inner part of the solid.

In this connection it may be pointed out, that the solubility, isomorphous miscibility, etc., in the surface layer of a crystal, should have other values than those for the inner part of the crystal, because the density of the surface layer must be different from that of the inner part. The lattice distance for the outer three to five layers must be (as one can infer from the calculations of Lennard-Jones¹⁵ on the density of small crystals) for heteropolar crystals appreciably smaller and for homopolar crystals, appreciably larger than for the inner part. The effect can be estimated to be over 10 per cent. In addition, the continuous character of the change in density in the direction of the surface offers rich possibilities for surface isomorphism.

It is clear that this kind of adsorption, which one may designate as surface alloying, can take place so slowly that the process will become

⁷ *Z. Elektrochem.*, **35**, 561, 1929.

⁸ H. Ekstein and M. Polanyi, *Z. physik. Chem. B*, **15**, 334, 1932.

⁹ Two free (*i.e.*, anti-symmetrically coupled) valencies could only lead to an addition if accompanied by the formation of two new free valencies (a duplication of the process described in the preceding paragraph).

¹⁰ *J.A.C.S.*, **38**, 2221, 1916; Langmuir and Kingdon, *Physik. Rev.*, **24**, 570, 1924.

¹¹ *Z. Elektrochem.*, **35**, 561, 1929.

¹² *J.A.C.S.*, **53**, 2168, 1931.

¹³ Davisson and Germer, *Physik. Rev.*, **30**, 705, 1927; E. Rupp, *Ann. Physik* (5), **5**, 453, 1931.

¹⁴ The structure of chabazite experiences also, according to the X-ray observations of M. S. Evans, an irreversible derangement when it absorbs a gas.

¹⁵ *Z. Kristallogr.*, **75**, 215, 1930.

measurable. The process of slow adsorption of ions on precipitates established by O. Hahn and L. Imre¹⁶ provides an example for this. Also some of the cases of activated adsorption pointed out by H. S. Taylor may belong to this group. The conception of this slowly forming surface solution is of course to be distinguished from the ordinary process of solution, which is assumed to be responsible for activated adsorption by A. F. H. Ward.¹⁷

3. Dispersion Forces.

The attraction discovered by S. C. Wang,² which was recognised by him to be a cohesive force, the concept of which has been amplified by F. London³ to form a general basis for molecular cohesion, I would like to designate here, on account of its close relation to the dispersion of light, as "dispersion force."

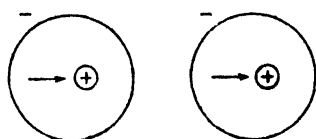


FIG. 3.—Identically directed polarisation as a cause of molecular attraction.

This force arises from the fact that two particles attract each other when both of them experience a polarisation in the *same* direction, as illustrated in Fig. 3, which has been taken from a previous communication in which the assumption of such forces was first suggested for the explanation of cohesion.¹⁸ This identically directed polarisation of the

two particles occurs (under the assumption of stationary charges, as can be easily shown) only when the electrical energy $-\frac{\mu^2}{d^3} = -\frac{(F\alpha)^2}{d^3}$

is larger than the energy $2\left(\frac{F^2\alpha}{2}\right)$ stored up in the interior of the particles,

thus only if $d < \sqrt[3]{\alpha}$. (μ = induced electrical moment of the particle, d = distance between the particles, F = field strength, α = polarisability.) Since, however, for two molecules or rare gas atoms under ordinary conditions d is larger than $\sqrt[3]{\alpha}$,¹⁹ this effect cannot occur, when the charges are stationary.

But an attraction does occur at all distances on account of the zero point vibration, when the latter accidentally causes the polarisation vectors to swing in the same direction. The origin of lower energy terms caused by the mutual approach of two polarisable particles can thus be visualised by the conception that the vibrations of the polarisation vectors of the neighbouring particles are statistically favoured, when the vectors are in the same direction.²⁰

The nature of the adsorption, which is governed by the dispersion force, and which is exerted by a solid adsorbent on a gas molecule has been derived by F. London and the author.²¹ It appears that:—

(1) The adsorption potential can be ascertained by simply summing

¹⁶ See e.g., *Z. angew. Ch.*, **43**, 875, 1930.

¹⁷ *Proc. Roy. Soc.*, **133A**, 506, 1931.

¹⁸ *Z. Elektroch.*, **26**, 372, 1920.

¹⁹ Not so for metal atoms: see K. F. Herzfeld (*Physic. Rev.*, **29**, 701, 1927), who connects this circumstance with electrical conductivity.

²⁰ This formulation of the theory of Wang and London I owe to a lecture of E. Wigner.

²¹ *Naturw.*, **18**, 1099, 1930; *Z. physik. Chem.*, **11B**, 222, 1930.

the attractive potential $\frac{c}{R^6}$ of one of the molecules adsorbed on the wall in relation to the single atoms of the wall,

$$\Phi = \iiint \frac{c}{R^6} N dv = \frac{N\pi c}{6} \frac{1}{r^3} \quad (1)$$

Φ = adsorption potential at the distance r from the wall, R = distance of the adsorbed molecule from the different atoms of the adsorbent. The constant c can be determined from the dispersion curve of the adsorbent and adsorbate according to the method given by London.³ An approximation is given by

$$c = \frac{3\alpha\alpha'}{2} \frac{II'}{I + I'} \quad (2)$$

where α and α' are the polarisabilities and T and T' the ionisation potentials of the gas molecules and the wall atoms respectively.

(2) The potential is not essentially dependent upon temperature. An influence due to orientation occurs (and therefore the effect of heat movement arises) only with the larger molecules.

(3) The potential at every point is independent of whether or not the neighbouring space is empty or occupied by a molecule.

(4) The molecules which are in the adsorbed state exert approximately the same force on one another as they do when they are free.

The last-mentioned three characteristics give to the adsorption potential of the dispersion force a very simple character and one which is quite similar to gravitation. It is an adsorption field of the kind assumed by the so-called "potential theory" which we will discuss later on.

A substantial success of the theory of dispersion forces lies in the fact that it provides up to now the only explanation for the parallelism between the adsorption potential of different gases and their condensibility. This parallelism, which has already been recognised by S. Arrhenius,²² finds its quantitative expression²³ in the comparison of the adsorption potential with the square root of the van der Waals' constant a . The fact that the adsorption forces of Ar, N₂, O₂, CH₄, CO₂ on charcoal are parallel throughout with the forces which are effective between like particles of these substances, shows that the cohesive forces of all these gases as well as the forces by which they are adsorbed, are all of the same nature. Since a rare gas appears in this series of substances it follows that the cause of general cohesion, which is also the cause of adsorption, must be the same attractive force which is effective between the atoms of the rare gas. And, since until now there exists no explanation for the cohesion of rare gases, except that proposed by the theory of S. C. Wang and F. London, we must assume this theory to give the general basis of cohesion and adsorption.

Actually it follows directly out of this theory that for the same adsorbents ($\alpha' = \text{const.}$, $I' = \text{const.}$) Φ is approximately proportional to \sqrt{a} , since according to F. London, the value of \sqrt{a} is chiefly determined by the magnitude of α .

²² S. Arrhenius, *Medd. Nobelinst.*, 2, 7, 1911.

²³ Z. *Electrochem.*, 26, 372, 1920. The way in which the adsorption potential was determined here brings with it the choice of a certain kind of adsorption forces, namely, of those which are effective, at higher coverings of the surface. (See next Part, Section 3.)

4. Capillary Condensation.

At this point it is convenient to insert some remarks about capillary condensation. When a porous body stands in contact with the vapour of a liquid whose saturation vapour pressure is p_0 , and which in the liquid state has the surface tension σ and the molecular volume V , the vapour condenses in the pores of the adsorbent at the pressure $p < p_0$ according to Thomson's equation,

$$RT \ln \frac{p_0}{p} = V\sigma \left(\frac{1}{r_1} + \frac{1}{r_2} \right) \quad (3)$$

where r_1 and r_2 are the two radii of curvature of the condensed liquid. However no quantitative agreement with this formula has ever been found when applying it to adsorption. But this does not exclude the effect of capillary condensation playing a rôle in adsorption. For in the case of an adsorbent with very narrow pores the effect may be combined with true adsorption and may assume a quantitative form essentially different from Thomson's equation.

Thus the part played by capillary condensation must be regarded in a general form: we must enquire how far at all the presence of a surface tension in the adsorbed material brings about a decrease in the equilibrium pressure over the adsorbent. We will return to this question later.

Part II.—The different ranges of adsorption and their mathematical treatment.

1. Highly Dilute Range.

All three kinds of adsorption forces which we have adduced above, the electrical field, the valencies and the dispersion forces, can be conceived of as potential forces. Accordingly the adsorbed amount, x , is proportional to the molecular density of the gas p/RT and the integral of the Boltzmann factor extended over all phase elements of the adsorption field.

$$x = \frac{p}{RT} \int e^{q/RT} \cdot dv, \quad (4)$$

where q is the average potential energy of the adsorbed molecules in the volume element dv .²⁴ The curved form of the adsorption isotherm is due then to the dependence of q on x , which is caused by the molecules which are already adsorbed exerting a repulsion or attraction on those which come up to them. This effect can only be neglected in the range where the layer is very thin. Here the integral $\int e^{q/RT} dv$ has a constant value and all isotherms become straight lines.²⁵

When one leaves aside the generally small effect of quantisation, leading to a deviation from equipartition, the heat of adsorption at every point is equal to the average potential energy of the adsorbed molecule, and the molar heat of adsorption w is given by

$$w = \frac{\int q e^{q/RT} \cdot dv}{\int e^{q/RT} \cdot dv} \quad (5)$$

and for the range of linear isotherms $w = \text{constant}$.

²⁴ One says that the molecule is in the volume element dv when a definite point of reference, e.g., the nucleus of a definite atom is within this volume.

²⁵ A. Eucken, *Verh. [dtsch. physik. Ges.]*, 16, 345, 1914.

These simple features of the highly diluted range, which are represented in Fig. 4, have been obtained up until now only in a few cases with certainty. A Magnus and H. Kratz²⁶ found that after thoroughly removing the oxide constituents from wood charcoal the isotherms for CO_2 at normal temperature were straight lines up to a pressure of about 1 mm. of Hg and that the molar heat of adsorption was in this range constant.

The slope of the linear isotherm as well as the heat of adsorption are dependent upon the temperature. When the temperature is increased the slope becomes less and at the same time the heat of adsorption decreases—and this to a remarkable degree.²⁶

If the distribution of the potential energy in the adsorbing field were known, that is the function $q(v)$, then x could be calculated from w and also the dependence of both magnitudes on the temperature could be predicted. An attempt to do this was made by A. Eucken,²⁵ however, without definite success.

New work in this field has emphasised the circumstance that the space in which high values of q exist is very small compared to that in which q has a smaller value. This appears not only in the comparison of different parts of the same adsorbent²⁷ but also by comparing different substances on the same adsorbent.²⁸ It seems to me, that the strong decrease in the heat of adsorption with temperature, mentioned above, also can be explained by such a distribution of the adsorption potential.

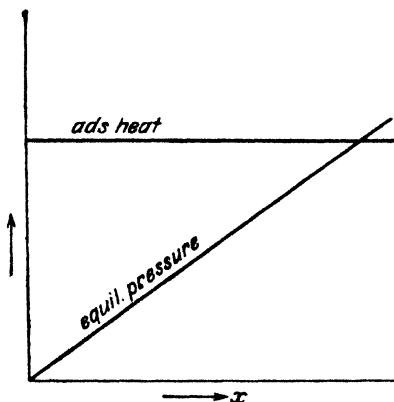


FIG. 4.—Highly dilute range of adsorption (pressure linear, heat constant).

2. Transition to a Larger Covering.

This question of the distribution of the potential in the adsorption field plays a decisive rôle in the domain of higher adsorption. We know that the various parts of the surface of the adsorbent send out adsorption forces of very different strengths.²⁹ How far this is due to the presence of electrical centres or surface valencies and how far it is caused merely by the roughness of the surface, would appear in a comparison of the adsorption of molecular gases with that of rare gases. However, I do not know of observations in regard to this point.

On account of our lack of definite knowledge of the composition and state of the surface we will here discuss two limiting cases which seem to represent two important types:

In the first case, we will assume that the centres of strongest adsorption lie so widely scattered in the surface that the mutual attraction force between the molecules adsorbed on these centres is to be neglected.

²⁶ A. Magnus and H. Kratz, *Z. anorg. allgem. Chem.*, **184**, 241, 1929.

²⁷ M. Polanyi and K. Welcke, *Z. physik. Chem.*, **132**, 371.

²⁸ M. Dunkel and H. Mark, *Wiener Akademieber.*, Abt. II., **138E**, 764, 1929.

²⁹ Garner and Blench, *J.C.S.*, **125**, 1288, 1924; Beebe and Taylor, *J.A.C.S.*, **46**, 143, 1924; A. Magnus and W. Kälberer, *Z. anorg. allg. Chem.*, **164**, 345, 1927.

In the second case (which we will discuss in the next section) an adsorbing space in the form of a slit or fissure is assumed. Here the adsorption force is a maximum at the apex and continually decreases in strength in the direction towards the mouth.

The first case corresponds to the assumption of Langmuir.³⁰ It leads, if all the centres of force have the same potential q^* and the same effective range v^* , to the Langmuir isotherm:

$$x = \frac{c_1 c_2 p}{1 - c_2 p}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

wherein c_1 is the number of centres and $c_2 = v^* \cdot e^{q^*/RT} \cdot \frac{p}{RT}$. One always obtains similar equations when one assumes an equal potential for all adsorbed molecules and at the same time neglects the mutual attraction between the adsorbed molecules.³¹ These assumptions, however, seem not to be realised for solid adsorbents. To be sure, the equation is frequently confirmed in the case of single isotherms by the arbitrary insertion of constants, but it always fails when one goes on further and investigates the dependence of the constants on the temperature.³²

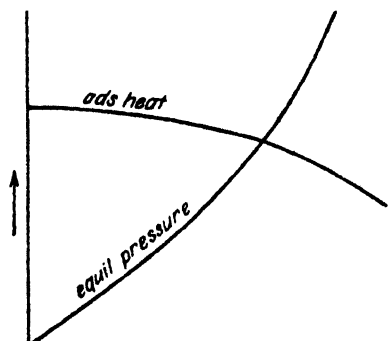


FIG. 5.—Transition to higher adsorption according to Langmuir's conception of stepwise saturation of isolated centres of various strength.

At the same time the inconstancy of the heat of adsorption shows, that the assumed equality of q^* is not fulfilled. This is because the force centres on a solid surface scarcely ever have equal values and also because the adsorption does not take place only on those isolated centres of force (single ions, single valencies) at which the effect of the mutual attraction of the adsorbed molecules can be neglected.

A case of isolated centres of equal force seems though to be realised in chabazite, according to the results of M. S. Evans,³³ on the sorption of ammonia by this mineral.

When we no longer assume that the centres of force are equal, then as Langmuir has already pointed out, an isotherm is to be expected which is made up of the sum of several such terms each of which, according to equation (6), holds for one group of equal centres. When the adsorption increases along such an isotherm the heat of adsorption gradually falls so that the total phenomena appear as in Fig. 5, which agrees frequently with experience. The Langmuir conception of an adsorption on isolated centres of force which, on passing from a highly diluted covering to a heavier one, become saturated step-wise may therefore be said to be very generally verified.

3. Range of Larger Covering.

When one considers the adsorption of a gas below its critical temperature, for example CO_2 at 0°C . on charcoal, one sees that the chief

³⁰ I. Langmuir, *J.A.C.S.*, 1917.

³¹ *Z. physik. Chem.*, 138A, 459, 1928.

³² See M. Volmer, *Z. physik. Chem.*

³³ *J.C.S.*, 1556, 1931.

adsorption takes place in the pressure range between 1 mm. and 1 atm. Within this range the adsorbed amount increases about a hundred times and thereby almost reaches the saturation value.

As was established in the first part of this survey this adsorption is probably governed by the dispersion forces.

When the surface is uniformly smooth the potential of these forces should decrease with the cube of the distance. On the other hand, for a porous adsorbent, which one may idealise as a fissure of molecular dimensions, this potential distribution may be very different. The potential surfaces in such a crack, resulting from the superposition of the

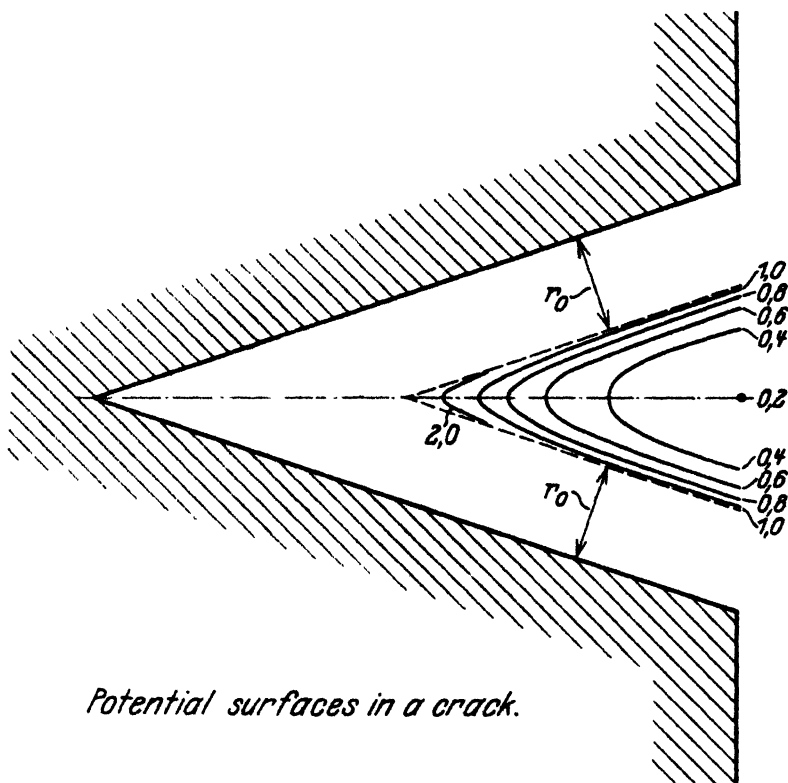


FIG. 6.—The potential in the interior of the crack is calculated by super position of the potentials c/v^3 of the two plane surfaces forming the walls of the crack.

c/v^3 functions of the two walls of the crack, are given in Fig. 6. The resultant distribution curve, $q(v)$, from which one can read the magnitude of the spaces which are to be assigned to the different potential ranges is shown as curve I. in Fig. 7. For comparison the curve $q = c/v^3$ which corresponds to a plane surface is also given (curve II.). The figure demonstrates how strongly fissuring is able to effect the distribution function $q(v)$. We shall see later that the $q(v)$ curve, which we have here calculated for a fissure, gives a plausible illustration of the state on an actual porous adsorbent, while in the case of (macroscopically) plane walls curves are obtained which are much more similar to the form $q = c/v^3$.

In order to utilise this conception of the adsorbent as a molecular fissure in which the potential of the dispersion forces prevails, we will introduce two idealising assumptions: (1) the potential of the dispersion force is assumed to be similar to gravitation; an assumption actually

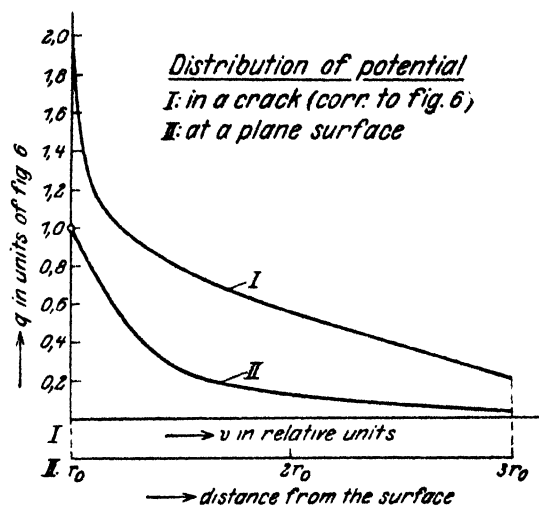


FIG. 7.

We can now imagine our adsorbent replaced by a vessel of macroscopic dimensions in which the same potential distribution $q(v)$ prevails as in the field of the adsorption forces. Then, with the aid of the fundamental equation of hydrostatics, we can calculate the amount of substance which the vessel will take up at equilibrium with any outside pressure, and we can consider this amount of substance as the amount adsorbed at the pressure under consideration.

The calculation is somewhat different for the cases above and below the critical temperature of the gas.

Above the critical temperature the expression

$$q = pv - \int_v^{v'} p dv + p'v' \quad (7)$$

is valid for every element of the vessel if p and v are the pressure and molecular volume of the gas in the outer space and p' and v' the same quantities for the space inside the vessel where the potential q prevails. From this formula one can eliminate the pressure by means of the equation of state which gives p as a function of density. Thus a function remains which gives for every value of the outside density (δ) a value of the density (δ') for the space under consideration in the vessel. By a summation over all the spaces one obtains finally the total amount of substance, $x = \int \delta' dv$, inside of the vessel. One can thus calculate every adsorption isotherm.

Below the critical temperature the same procedure is valid for all spaces in which no condensation occurs, that is, until the density calculated from (7) reaches the density of the saturated vapour. All spaces in which the potential has a higher value will be filled by liquid. It is easy also to take into consideration the compressibility of the liquid and then arrive at a precise calculation of the contents of the vessel, *i.e.*, the amount adsorbed.

permissible only for rare gases or very simply constructed molecules (see Part I., Sect. 3); (2) we will neglect all the complications which result from the narrowness of the adsorption space. One of these complications, the one namely which arises from the surface tension of the adsorbed film, we shall consider in the next section. Otherwise we will leave the assumption, that these complications can be neglected, to stand as a hypothesis, to be judged by experiment.

highest adsorption values of the lowest isotherm (on the dotted part of the curve) stand outside the theoretical relationship since this range of measurement does not occur in the other isotherms. But still the agreement appears to be very far-reaching.

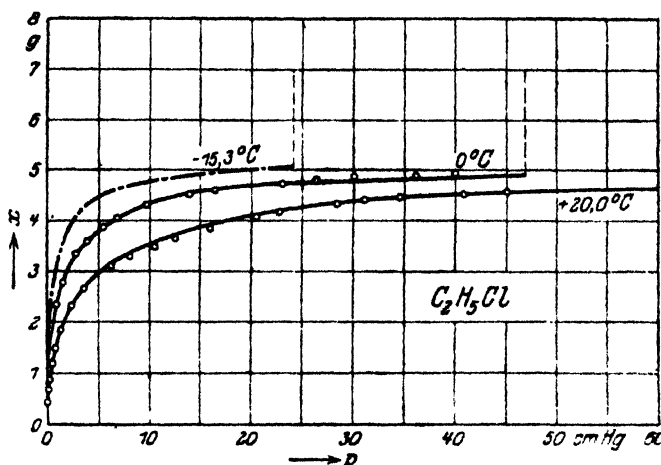


FIG. 8.—From the isotherm belonging to the temperature -15.3°C . the two other isotherms have been calculated (curves calculated, rings mark observations).

The potential distribution $q(v)$ determined according to the method indicated above, on which the calculations of the measurements of Titoff are based, is given in Fig. 11 as curve I. Its form, which other experience shows to be typical for porous adsorbents (charcoal and silica

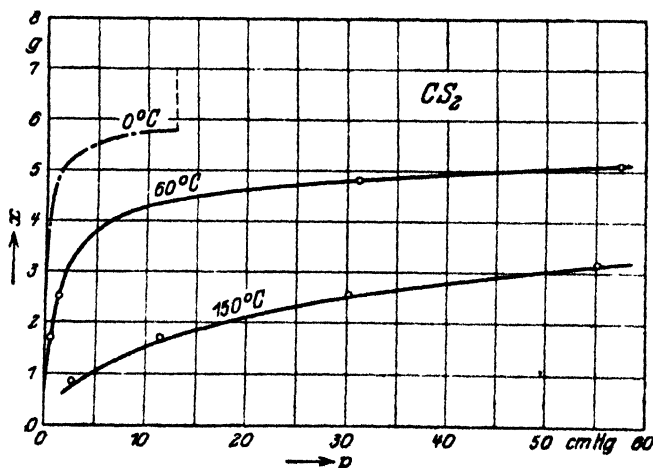


FIG. 9.—From the isotherm belonging to the temperature 0°C . the other two isotherms have been calculated (curves calculated, rings mark observations).

gel), has a similarity to the potential distribution of the molecular fissure (Fig. 7) so that one may assume a relationship between them. It is interesting to note that the adsorption on macroscopically plane quartz walls, which was investigated several years ago in collaboration with

H. Beutler,³⁷ shows a potential distribution which deviates quite widely from this, giving through equation (10) the curve II. in Fig. 11. This latter is rather similar to curve II. in Fig. 7 which corresponds to a plane surface.

We can extend these considerations to the adsorption of two substances *A* and *B* on different forms of the same adsorbent: the potentials $\frac{C_A}{r^3}$ and $\frac{C_B}{r^3}$ should indicate the potentials of *A* and *B* respectively on a plane surface of the adsorbent. Now take the same adsorbing material, for example charcoal, used in two geometrically different forms, i.e. in two different degrees of porosity. In this case for each of these samples (Nos. 1, 2, ...) a different distribution of potential $q_1(v)$, $q_2(v)$, ... holds, and these again are different for *A* and for *B*. However, as is easily seen, the relationship,

$$\frac{(q_1(v))_A}{(q_1(v))_B} = \frac{(q_2(v))_A}{(q_2(v))_B} = \dots = \frac{C_A}{C_B} \quad (12)$$

will always remain valid. Therefore it follows, according to equations (10) that

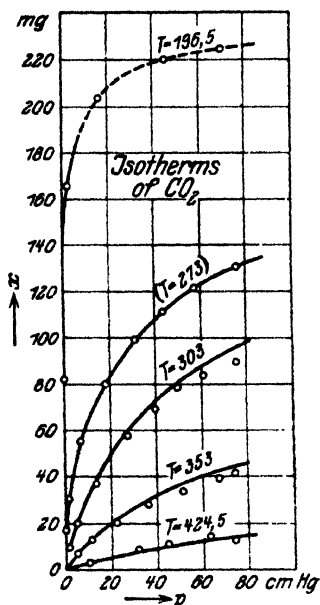


FIG. 10.—From the isotherm belonging to $T = 273$ the other four isotherms have been calculated.

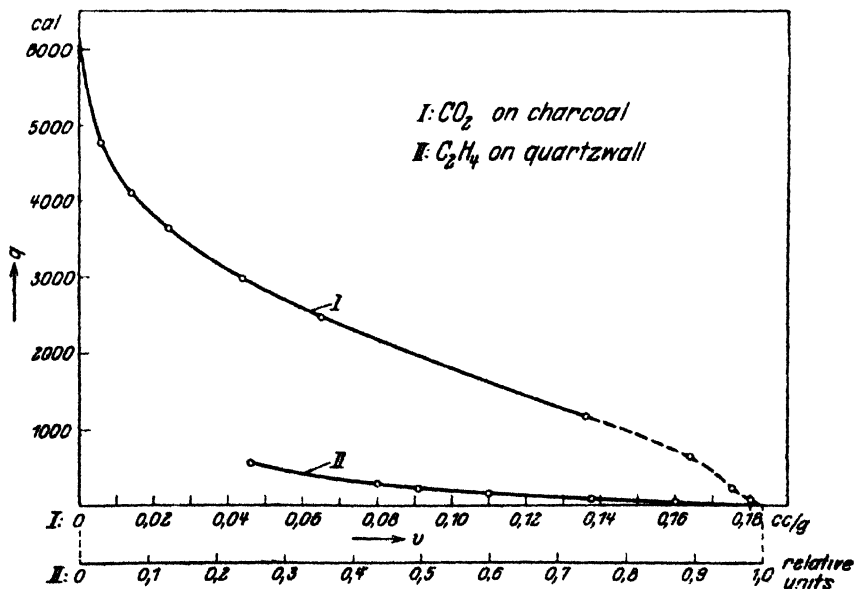


FIG. 11.—Curve I. Potential distribution related to the isotherms in Fig. 10. Curve II. Potential distribution calculated from an isotherm of ethylene on a smooth quartz wall.

³⁷ In this yet unpublished work the isotherms of C_2H_4 were measured at the temperature of liquid air and liquid oxygen, following them up to the pressure of the saturated vapour.

on comparing the adsorption of two substances A and B on different samples 1, 2, . . . one should always find for equal values of χ/δ^* and equal temperatures the same ratio. That is the relationship found by P. Kubelka.³⁸ We prefer to derive it in this way from the potential theory instead of from the capillary theory, since, as will be seen in the next section, the capillary condensation predominates only in the neighbourhood of the saturation pressure whereas the relation of Kubelka holds over a much larger range.

Another point to be mentioned is this: According to the potential theory, expanded above, the adsorbed vapour goes over into the condensed state as soon as the saturation density is reached. Above the critical temperature an analogous phenomenon is to be expected in the

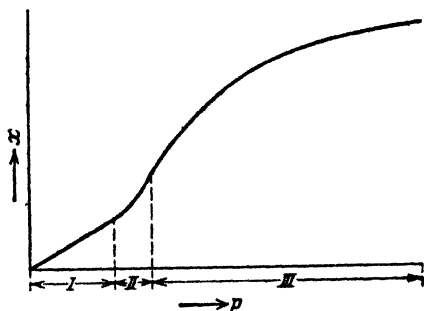


FIG. 12.—Schematic diagram of the adsorption curve according to potential theory.

Section I.—Highly dilute range (linear).

Section II.—Curvature caused by the action of the cohesive forces in the adsorbed film.

Section III.—Portion tending to saturation.

range where the density of the gas increases faster than the pressure because of the action of the van der Waals' cohesive forces. Only above this range will the action, due to the b constant predominate, which works in the opposite direction. Hence the isotherms should have in general a form like the one shown in Fig. 12 which is taken from a previous communication.³⁹ After the linear portion of the isotherm at the beginning, a bending toward the ordinate should follow, which corresponds to the predominance of the cohesive forces (condensation in case of vapours), and then only would

the ordinary curvature of the adsorption isotherm set in.

It is known that the investigations of Langmuir⁴⁰ and N. K. Adam⁴¹ gave ample proof of condensation occurring in surface films of fatty acids. A condensation effect has also been shown by A. Frumkin to occur in the case of adsorption of soluble substances at the interface liquid-gas.

In the case of adsorption on solid surfaces the concavity towards the x -axis, which would correspond to condensation, is usually overbalanced by the opposite bending caused by the saturation of the stronger adsorbing centres (see Part I, Fig. 5). Nevertheless, this concave curvature could be demonstrated in one case, namely in a series of experiments, done in collaboration with C. Welcke,⁴² on the adsorption of SO_2 on technical charcoal. A strong argument for assuming that there is actually a condensation effect present here, is offered by the circumstance that the curving of the adsorption isotherm is accompanied by an increase in the heat of adsorption amounting about to the heat of condensation. Besides the curving appears in a range of adsorption where it could be theoretically expected. Other measurements carried out on

³⁸ Koll. Z., **55**, 1, 1931; Z. Electrochem., **37**, 637, 1931.

³⁹ Verh. deutsch. physik. Ges., **18**, 55, 1916.

⁴⁰ J.A.C.S., **1848**, 1917.

⁴² Z. physik. Chem., **132**, 321, 1928.

⁴¹ Proc. Roy. Soc., 1921-1929.

ash-free charcoal failed to show the above effect.⁴³ It is difficult to say how far the remarkable results of A. J. Allmand and L. C. Burrage⁴⁴ can be explained in this connection.

4. Neighbourhood of Saturation.—Different effects caused by the surface tension of the adsorbed vapour.

On approaching the saturation pressure of a vapour there occurs in the pores of the adsorbent a condensation due to the Thomson effect. The question as to how far the range of capillary condensation extends is still under discussion. We have already (at the end of Part I.) mentioned that the chief difficulty lies in the circumstance that the Thomson formula does not seem to hold and therefore the question must be put in a general form by asking, how much the vapour-pressure of a liquid in the pores of an adsorbent is lowered by the action of the surface tension.

On examining this question, it appears⁴⁵ that the existence of surface tension in general does not lower, but raises the vapour tension, of an adsorbed layer. Only in the case of several adsorbed layers, and only when they are on the inside of pores, does a lowering occur. Since both effects of the surface tension are of importance to us we will discuss them here together.

In order to spread out a mole of a liquid into a thin layer of the thickness Δ one must produce a free surface which in size is equal to v/Δ and perform work equal to

$$u = \sigma \cdot 2 \frac{v}{\Delta} \quad (13)$$

(σ = surface tension). The thin layer has therefore a vapour tension p_{Δ} which is larger than the normal saturated pressure p_0 according to the formula,

$$RT \ln \frac{p_{\Delta}}{p_0} = \sigma \frac{2v}{\Delta} \quad (14)$$

(This is essentially the Thomson relationship.)

For layers of molecular thickness it is to be assumed that the surface tension is smaller than the normal value. If one at first neglects this difference, one gets, e.g., for ethyl ether at 0° C. for $\Delta = 5.5 \text{ \AA}$, $\sigma = 15 \text{ ergs}$, $v = 100$,

$$u = RT \ln p_{\Delta}/p_0 = 1300 \text{ cal.} \quad (15)$$

Thus for a monomolecular layer the vapour pressure is raised about ten times.⁴⁶

⁴³ A. Magnus, H. Giebenhain und H. Velde, *Z. physik. Chem.*, **150**, 285, 1930.

⁴⁴ *Proc. Roy. Soc.*, **130**, 610, 1931.

⁴⁵ *Verh. deutsch. physik. Ges.*, **18**, 55, 1916.

⁴⁶ That means, that the formation of a monomolecular layer would be possible at the saturation pressure only if the adsorption potential was larger than u . Hence for vapours of metals, the surface tensions of which are several hundred ergs, a monomolecular layer could be formed at the saturation pressure only if the adsorption potential had enormous values of the order of 100,000 calories. This accords with the phenomena observed by M. Knudsen und R. W. Wood, that have been discussed by Chariton, Semenoff and Shalnikoff at this meeting. In these cases the adsorption potential can mostly be neglected in comparison with u , so that the vapour density at which condensation of the metals (and other substances of similarly high surface tension) should necessarily occur, could be estimated by equation (15), in assuming $u \cong 100,000$. However, the vapour densities at which condensation actually occurs, lie far below the limits estimated in this way.

The increase u of the free energy of the adsorbate, which is caused by its spreading out in a thin layer persists also when the film lies in the interior of a fissure. If the potential in the crack amounts to q , then

$$RT \ln p_0/p_\Delta = q - u. \quad (16)$$

Hence, when the adsorption potential is calculated by means of equation (10a), one obtains actually not q but $(q - u)$. Taking into account the fact that we probably have markedly overrated the value of σ for a monomolecular film, we may estimate the error caused by taking $(q - u)$, instead of q for ethyl-ether at 0° to be about 1000 cal. With increasing temperature the error becomes smaller, and on approaching the critical temperature almost disappears. Hence the calculated value of $q(v)$, instead of

being constant, should decrease somewhat with increasing temperature,—an effect actually found by experience.³⁴

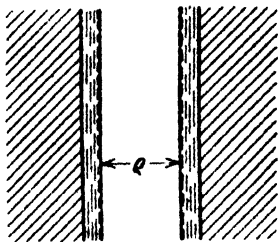


FIG. 13.

layer of liquid, with a distance ρ between the two layers (Fig. 13) then the work, which is gained when one brings a mole of the liquid into the fissure, which it entirely fills, is equal to the simultaneous decrease of the surface energy

$$u' = \sigma \cdot 2 v/\rho \quad (17)$$

and consequently we have for the vapour pressure p_ρ of the liquid, that fills the gap of the width ρ , the relation

$$RT \ln p_0/p_\rho = u' = \sigma \times 2 \times v/\rho \quad (18)$$

In this the potential arising from the walls is of course disregarded. If we assume the value of this potential in the gap between the two films to be q , the equilibrium pressure p of the substance adsorbed in the gap would correspond to the relation

$$RT \ln p_0/p = q + u' = q + \sigma \times 2 \times v/\rho \quad (19)$$

which shows that the potential calculated by the equation (10) would exceed the correct value by the amount u' .

In estimating the magnitude of u' we have to keep in mind that the surface tension σ of the two liquid films separated by the distance ρ disappears, when ρ goes to zero. There is therefore a limit to u' , which would about be reached when ρ is brought down to a molecular diameter. This gives us, e.g., for ethyl-ether at 0° C., $u' = 1300$ cal., corresponding to a depression of the equilibrium pressure to $1/10$.

With rising temperature u' falls off and practically disappears midway between the boiling-point and the critical temperature. Upwards from this region of temperature the influence of capillary condensation can be completely neglected for adsorptions at ordinary pressures.

In conclusion we may deduce from this last section, that the influence

of the surface tension of the adsorbed film leads to two effects of contrary directions, the free energies of which we have denoted above by u and u' . These two magnitudes (the latter of which stands for the capillary condensation) superpose themselves to the adsorption potential and can cause marked deviations from the idealisation discussed in the previous section. They practically disappear, however, at higher temperatures, where a fairly wide field exists, in which they can be left out of consideration.

*Berlin Dahlem,
Kaiser Wilhelm Institut für physikalische Chemie.*

PROCESSES OF ADSORPTION AND DIFFUSION ON SOLID SURFACES.

BY J. E. LENNARD-JONES (*Bristol*).

Received 4th January, 1932.

§ 1.

The literature pertaining to the sorption of gases by solids is now so vast¹ that it is impossible for any, except those who are specialists in the experimental technique, rightly to appraise the work, which has been done, or to understand the main theoretical problems which require elucidation. The author has been fortunate in this respect in having the benefit of the experience of Professor Garner, who has brought to his attention from time to time many of the problems relating to sorption and has sifted the experimental material for this purpose. The ideas in this paper have been stimulated by these discussions and it seemed appropriate to bring them forward tentatively for discussion at this meeting.

As the author understands it, one of the main problems which recent work has emphasised is the nature of the cohesion which holds gases to solid surfaces, and whether molecules are held as molecules or dissociated into atoms. The same gas and the same solid appear in certain cases to interact in a different way according to the temperature. In the case of hydrogen and certain metals, for instance, there is considerable adsorption at very low temperatures, then the adsorption diminishes to a minimum at temperatures between -180° and 0° , increases to a maximum and then diminishes again at high temperatures.² Garner³ has found in some cases evidence that there is still another increase of adsorption at very high temperatures. There appear to be at least three different kinds of adsorption.

The first type (that at low temperatures) is usually ascribed to van

¹ Cf. the comprehensive and authoritative volume, which has just been published by J. W. McBain, *The Sorption of Gases and Vapours by Solids* (Routledge, London, Jan., 1932).

² Benton and White, *J.A.C.S.*, **52**, 2332, 1930; Taylor and Williamson, *J.A.C.S.*, **53**, 2168, 1931; Taylor and McKenney, *J.A.C.S.*, **53**, 3604, 1931; cf. also McBain, *loc. cit.*, 306-321.

³ Garner and Kingman, *Nature*, **126**, 352, 1930; *Trans. Far. Soc.*, **27**, 322, 1931.

der Waals' forces, though actual quantitative calculations of the heats of adsorption due to such forces have been worked out in very few cases. In § 2 an attempt is made to extend the scope of these calculations, and the interaction of an inert gas atom and a metal is worked out.

The second type of adsorption has been called chemisorption by some, "activated" adsorption by others, but no theory of its nature has been put forward in terms of the electronic structure of the solid and the adsorbed atom. In § 3 a qualitative theory is proposed for this type with special reference to hydrogen on metals such as nickel and copper. It is suggested that the hydrogen is dissociated into atoms, and for this process to occur a certain "activation" energy is necessary. The non-occurrence of this type of adsorption at very low temperatures may then be readily understood. A similar theory could be constructed for other molecules though it is not necessary that a molecule should be completely dissociated. As in all cohesion problems the governing principle is one of energy. The molecule and the approaching molecule will tend to assume that form in which the total energy is a minimum. If the bond of a molecule is very strong (as in nitrogen), dissociation may not occur, and adsorption at room temperatures may be negligibly small.⁴

In addition to the instantaneous adsorption of gases on the outer surface of a solid, it has been known for some time that a slow sorption also occurs and this has been attributed to the diffusion of the gas into the interior of the solid. This has sometimes been referred to as a solution process, sometimes as a diffusion along the cracks of the solid into the interior, but a kinetic theory of the mechanism does not appear ever to have been worked out. An attempt at a theory is made in § 4 and applied to the recent beautiful results of Ward⁵ on the slow sorption of hydrogen by copper. Ward has succeeded in separating the two processes of rapid and slow sorption, and finds that slow sorption has an energy of activation as well. The theory here suggested gives a simple interpretation of this quantity. It appears that there may be an activation energy for *adsorption* and another quite different one for slow sorption or *absorption*.

§ 2. Adsorption Due to Van Der Waals' Forces.

(1) **Van Der Waals' Fields Outside Metals.**—Although there is now a vast amount of experimental material as to the energy of adsorption, theoretical calculations have been made in very few cases, and as the order of magnitude of the energy of adsorption is often used as a criterion of the nature of the adsorption, it seems desirable to push the theoretical work as far as possible in this direction. A calculation giving only orders of magnitude of the energy of adsorption may be a useful guide in interpreting experimental results. Such a calculation was given for the first time by the author and Miss Dent⁶ at a Discussion of the Faraday Society four years ago. It was shown that the attraction of a crystal of KCl on an argon atom outside it due to the van der Waals' forces was sufficient to give a heat of adsorption of the order of 2000 cal. per gram atom. Other calculations of a similar kind have since been made and

⁴ Cf. Schmidt, *Z. physik. Chem.*, **133**, 295, 1928, who found that the adsorption of nitrogen on nickel was very small; cf. also Dew and H. S. Taylor, *J. phys. Chem.*, **31**, 281, 1927.

⁵ Ward, *Proc. Roy. Soc.*, **133A**, 506 and 522, 1931.

⁶ Lennard-Jones and Dent, *Trans. Far. Soc.*, **24**, 100, 1928.

lead to results of the same order.⁷ It would be useful if, for purposes of comparison, experimental determinations could be made of heats of adsorption of an inert gas such as argon on a crystal of the KCl type. The experimental conditions are difficult, however, because of the small surface area presented by such a crystal per unit mass. It seems desirable therefore to extend the calculations of the effect of the van der Waals' fields to other surfaces more amenable to experimental investigation. In this paragraph I attempt to estimate these fields outside a metal.

During the last year or two considerable progress has been made towards an understanding of the nature of the Van der Waals' fields, and it is now possible in the case of some inert gases to deduce from their electronic structure the forces they exert on each other.⁸ It is now definitely established that atoms attract each other at large distances according to an inverse seventh power law. The attraction seems to be

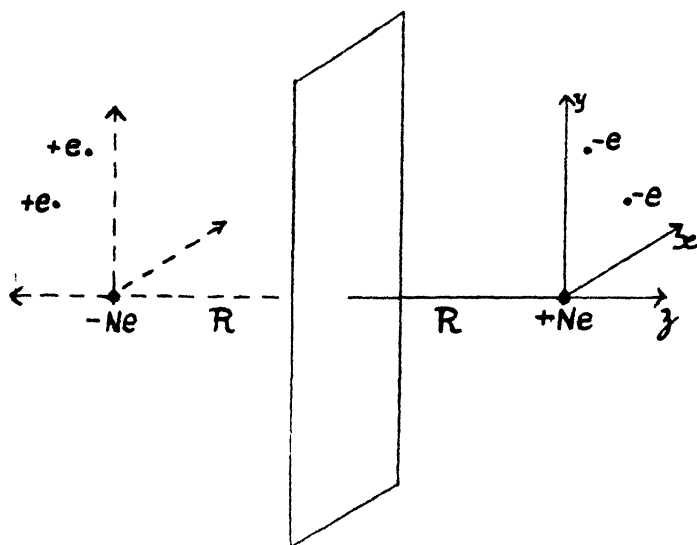


FIG. 1.—An atom and its electrical image.

due to a sympathetic fluctuation of the electron space clouds of the two atoms, which produces in the atoms effective dipoles tending to move more in phase than out of phase.

The classical picture of a metallic conductor is a continuum of electric fluid which is so mobile that its surfaces may be regarded as equipotentials, and this picture is to some extent restored by the modern theories of Bloch and others. The conduction electrons constitute a very mobile electric fluid extending throughout the metal, and so a metal may be regarded as a perfectly polarisable system.

This picture justifies the classical method of electrical images in calculating the interaction of a charge and a metallic conductor, and may be used when the charge is at such distances from the metal that its atomic constitution is not important. We shall therefore suppose that when an atom or molecule is brought adiabatically from an infinite

⁷ London, *Z. physik. Chem.*, **11**, 222, 1930.

⁸ Cf. a recent lecture on Cohesion by the author, *Proc. Lond. Phys. Soc.*, **43**, 461, 1931, where references are given.

to a finite (though large) distance from a metallic conductor, the effect on it is the same as that of its electrical image in the surface of the metal.

Let the nuclear charge of the atom (supposed neutral) be N , and let the co-ordinates of the electrons referred to perpendicular axes through the nucleus be $(x_1, y_1, z_1) \dots (x_r, y_r, z_r) \dots (x_N, y_N, z_N)$, where the z axis is taken in the direction of the outward drawn normal to the surface of the metal. If the wave functions of the electrons in the atom to be $u_1, u_2 \dots u_N$, the wave function of the whole atom may be written

$$\Psi = 1/(N!)^{\frac{1}{2}} \begin{vmatrix} u_1(1) & \dots & u_r(1) & \dots & u_N(1) \\ \vdots & & \vdots & & \vdots \\ u_1(N) & \dots & u_r(N) & \dots & u_N(N) \end{vmatrix}$$

where $u_r(s)$ represents the function obtained by substituting the co-ordinates of the s th electron (x_s, y_s, z_s) and its spin co-ordinate) in the r th wave function. Each component wave function is supposed normalised and orthogonal to the rest.

If R is the distance of the nucleus from the surface of the metal, the co-ordinates of the electrical images of the electrons referred to the same co-ordinate axes are $(x_1, y_1, -2R - z_1)$, etc., while those of the nucleus are $(0, 0, -2R)$. The image has a nuclear charge of $-N$ and N positive charges surrounding it.

If R is large, the atom and its image may each be represented by N dipoles and the mutual potential energy is

$$v = -e^2/(2R)^3 \sum_{r,s} (x_r x_s + y_r y_s + z_r z_s).$$

The potential energy of the atom due to its image is thus

$$\begin{aligned} W &= -e^2/(2R)^3 \int \bar{\Psi} \left(\sum_{r,s} (x_r x_s + y_r y_s + z_r z_s) \right) \Psi d\tau_1 \dots d\tau_N, \\ &= -e^2/(2R)^3 \int \sum_{r,s} (x_r x_s + y_r y_s + z_r z_s) \rho d\tau_1 \dots d\tau_N, \end{aligned}$$

where

$$\rho = 1/N! \begin{vmatrix} \rho(1, 1) & \dots & \rho(1, N) \\ \vdots & & \vdots \\ \rho(N, 1) & \dots & \rho(N, N) \end{vmatrix},$$

and

$$\rho(1, 2) = \sum_i \bar{u}_i(1) u_i(2),$$

and the integration is taken over the whole space of each electron. The summation is over every pair of r and s including $r = s$.

Now it can easily be shown* that

$$\begin{aligned} \int \rho d\tau_1 \dots d\tau_{r-1} d\tau_{r+1} \dots d\tau_{s-1} d\tau_{s+1} \dots d\tau_N &= 1/N(N-1) \begin{vmatrix} \rho(x_r, x_r) & \rho(x_r, x_s) \\ \rho(x_s, x_r) & \rho(x_s, x_s) \end{vmatrix} \\ \int \rho d\tau_1 \dots d\tau_{r-1} d\tau_{r+1} \dots d\tau_N &= \rho(x_r, x_r)/N, \end{aligned}$$

* Lennard-Jones, *Proc. Camb. Phil. Soc.*, **27**, 469, p. 475, 1931.

and hence

$$\begin{aligned} \int \sum_r (x_r^2) \rho d\tau_1 \dots d\tau_N &= \int x_r^2 \rho(x_r, x_r) d\tau_r = \sum (x^2)_{l, l} \\ \int \sum_{r, s}' (x_r x_s) \rho d\tau_1 \dots d\tau_N &= \int x_r x_s \left| \begin{array}{cc} \rho(x_r, x_r) & \rho(x_r, x_s) \\ \rho(x_s, x_r) & \rho(x_s, x_s) \end{array} \right| d\tau_r d\tau_s \\ &= 2 \sum_{l, m} \{x_{l, l} x_{m, m} - x_{l, m} x_{m, l}\}, \end{aligned}$$

where the last summation on the left does not include $r = s$, and the last summation on the right is over every pair of l and m . The quantities $x_{l, m}$ and $x^2_{l, l}$ are the matrix elements of x and x^2 with respect to the wave functions, thus

$$x_{l, m} = \int \bar{u}_l(x) x u_m(x) d\tau.$$

Now wave functions of an atom are symmetrical about the origin except as regards sign. Some functions are even, others odd. But clearly in every case $x_{l, m} = 0$ when $l = m$. Hence

$$\int \sum_{r, s} x_r x_s \rho d\tau_1 \dots d\tau_N = \sum_l (x^2)_{l, l} - 2 \sum_{l, m} x_{l, m} x_{m, l}.$$

Further $x_{l, m}$ is a measure of the transition probability of an electron from a state represented by u_l to one represented by u_m , and this probability is zero except between certain wave functions of one complete shell and certain of another. In argon, for instance, the only possible transitions are from $1s$ to $2p_{\pm 1}$ and $3p_{\pm 1}$, from $2s$ to $3p_{\pm 1}$, and from $3s$ to $2p_{\pm 1}$, and only between states of the same spin. These terms are thus less in number than those of the type $(x^2)_{l, l}$ and are not so great in magnitude. As a first approximation we shall neglect the products $x_{l, m} x_{m, l}$ and similarly the corresponding terms in y and z and write

$$\begin{aligned} \int \sum (x_r x_s + y_r y_s + z_r z_s) \rho d\tau_1 \dots d\tau_N &= \sum (x^2 + y^2 + z^2)_{l, l} \\ &= \overline{(x^2 + y^2 + z^2)} \end{aligned}$$

where the last quantity is a mean value taken over the total electron space charge of the atom.

The inert gas atoms are spherically symmetrical and we have $\overline{x^2} = \overline{y^2} = \overline{z^2} = \overline{r^2}/3$, so that

$$W = -e^2 \overline{r^2} / 6R^3.$$

The quantity $\overline{r^2}$ can be calculated when the electron distribution is known. The distributions given by Hartree may, for instance, be used for this purpose.¹⁰ It is possible, however, to deduce $\overline{r^2}$ from the magnetic susceptibility, for it is known that the susceptibility per gram atom (χ) is given by

$$\chi = -\{Le^2/6mc^2\} \overline{r^2},$$

¹⁰ Hartree, *Proc. Camb. Phil. Soc.*, 24, 89 and 111, 1928.

where L is Loschmidt's number (6.06×10^{23}), m is the mass of the electron and c is the velocity of light. We thus have the formula

$$W = \mu R^{-3}$$

where

$$\mu = mc^2\chi/L.$$

The attractive field of a metal on an inert gas atom at a large distance is therefore proportional to the magnetic susceptibility of the atom. This will not necessarily be true of the heats of adsorption, for the equilibrium distances will vary from gas to gas.

This result is true only for spherically symmetrical atoms, and may not be applied to molecules except to those which are reasonably spherical. It has, however, been tentatively applied to hydrogen, nitrogen, and carbon dioxide, as their internuclear distances are small and their rotations tend to increase the apparent symmetry. The results are included with some of the inert gases in the adjoining table.

TABLE I.—THE CONSTANTS (μ) OF THE ATTRACTIVE FIELD BETWEEN GASES AND METALS.

Gas.	Diamagnetic ¹¹ Susceptibility ($-\chi \cdot 10^6$).	μ in ergs (R in Å).	μ in cal./g. mol. (R in Å).
He . . .	1.88	$2.52 \cdot 10^{-12}$	$3.65 \cdot 10^4$
Ne . . .	6.66	$8.93 \cdot 10^{-13}$	$12.9 \cdot 10^4$
Ar . . .	18.13	$24.3 \cdot 10^{-13}$	$35.2 \cdot 10^4$
H ₂ . . .	3.9	$5.23 \cdot 10^{-12}$	$7.6 \cdot 10^4$
N ₂ . . .	7.4	$9.92 \cdot 10^{-13}$	$14.4 \cdot 10^4$
CO ₂ . . .	18.7	$25.0 \cdot 10^{-13}$	$36.2 \cdot 10^4$

It is not possible from these figures to deduce more than an estimate of the heats of adsorption until the short range repulsive forces have been calculated. In the meantime we may proceed somewhat as follows: the closest distance of approach of copper atoms in the metal is 2.54 Å ¹² while the closest distance of approach of argon atoms in the solid form is 3.84 Å .¹³ We may therefore suppose the equilibrium distance of argon from a copper surface to be (roughly) the mean of these two distances, *viz.*, 3.2 Å . Now the more detailed calculations carried out below show that at the equilibrium distance, the potential due to the repulsive fields is between one-third and one-half of that due to the attractive fields. If we allow 40 per cent. for the repulsive fields, we then find for the heat of adsorption of argon on copper about 6000 cal. per gram atom. A similar calculation for nitrogen on copper leads to about 2500 cal./gram mol., and that for hydrogen to about 1300 cal./gram mol. These are of the same order as those observed at very low temperatures.

(2) **Van der Waals' Fields outside Crystals.**—The calculations given in the preceding paragraph do not permit of a complete exploration of the potential field outside the surface. It will be impossible to do this until the atomic constitution of the metal can be taken into account. It seemed to the author desirable to supplement this work by considering another case where the exploration can be carried out in greater detail.

¹¹ Stoner, *Magnetism* (London, Methuen, 1930), 28 and 33.

¹² W. H. Bragg and W. L. Bragg, *Crystal Structure*, (1924), 163.

¹³ Simon and Simson, *Z. Physik.*, **28**, 160, 1924.

It is possible in theory to calculate van der Waals' fields between any two inert gas atoms, but the work becomes intractable in practice. Fortunately, however, it is possible to deduce information about these fields by other means. The author has deduced information about the fields of force between certain atoms from the equation of state. In the one case which has been considered in some detail by the methods of quantum mechanics and by the equation of state, namely, that of two helium atoms, the results are in very good agreement,¹⁴ although the mathematical formulæ used to represent the field seem very different. The potential field of two helium atoms deduced from electronic structure is given in the form¹⁵

$$\phi = \{7.7e^{-2.43r/a_0} - 0.68(r/a_0)^{-6}\}10^{-10} \text{ ergs,}$$

whereas that deduced from the equation of state is assumed to be of the form

$$\phi = (\lambda/\overline{n-1})r^{-n+1} - (\mu/\overline{m-1})r^{-m+1}. \quad (0.53 \text{ \AA.})$$

The a_0 in Slater's equation is the length of a Bohr orbit. It can be shown that the latter law represents the potential curve of the more elaborate formula given above in a remarkable way over the range of r , which is of interest. This may be taken as a justification of the inverse power laws and they may be used in the following investigation with some confidence.

The van der Waals' field of *force* between two argon atoms deduced from the equation of state¹⁶ has been shown to be $\lambda r^{-13} - \mu r^{-7}$, where $\lambda = (2.13) 10^{-102}$ and $\mu = (6.50) 10^{-58}$. Now the electronic structure of the K^+ and Cl^- ions of KCl is the same as that of argon, and we may suppose as a first approximation that they have the same van der Waals' fields. (Actually that of Cl^- will be greater and that of K^+ less than that of argon because the one is more polarisable and the other less polarisable than argon.) The method of calculating the attractive field outside a (1, 0, 0) plane of a KCl crystal has been given in a former paper⁶ and need not be repeated here. When that paper was written, the correct law for the van der Waals' attraction was not known and it was assumed to be of the type r^{-5} or r^{-6} . We now take it to be r^{-7} as is indicated by quantum mechanics.¹⁷

By similar methods the repulsive field has been calculated as well (again supposing the K and Cl ions to repel as argon atoms, which is only approximately true). The total field above a lattice point of KCl is shown in Fig. 2 curve (1). The minimum energy proves to be -0.76×10^{-13} ergs which corresponds to a heat of adsorption of 1100 calories per gram atom, and the equilibrium distance¹⁸ is $0.575a$, i.e., 3.61 \AA.

¹⁴ Cf. Lennard-Jones, *Proc. Lond. Phys. Sci.*, **43**, 475 and 476, 1931.

¹⁵ Slater, *Physic. Rev.*, **37**, 696, 1931.

¹⁶ Actually the equation of state does not determine the n of the repulsive field uniquely, but shows it to be of the order 10, 11 or 13. For any of these values of n , it then determines the λ and μ of the formula $\lambda r^{-n} - \mu r^{-m}$ uniquely. The calculations of this paragraph have been carried out for $n = 10$ and $n = 11$, as well as for the $n = 13$ given in the text, and have led to very similar results, cf. footnote 19.

¹⁷ This method is justified, as London has shown that to a close approximation Van der Waals' fields are additive (*Z. physik. Chem.*, **11**, 222, 1930).

¹⁸ If throughout the calculations n is assumed to be 10 or 11, the heats of adsorption are respectively 1200 and 1100 cal./gram atom and the equilibrium distances 3.69 \AA. and 3.67 \AA. The result obtained in the former paper (*loc. cit.*), assuming an attractive field of r^{-5} , was 2000-2500 cal./gram atom.

Similar calculations have been made for points above the centre of a lattice cell, and it has been found that here the attraction is greater and the potential field reaches its absolute minimum. The difference between this attractive curve and the one just referred to is considerable. The absolute minimum gives a heat of adsorption of 1600 cal./gram atom and a smaller equilibrium distance¹⁹ (3.08 Å). This fluctuation of the potential field over the surface of the crystal may be of some importance, as is shown in § 4. The potential field of NaF on a neon atom has been calculated by similar methods and the result is given in curves (3) and (4) in Fig. 2. The heat of adsorption is about 500 cal.

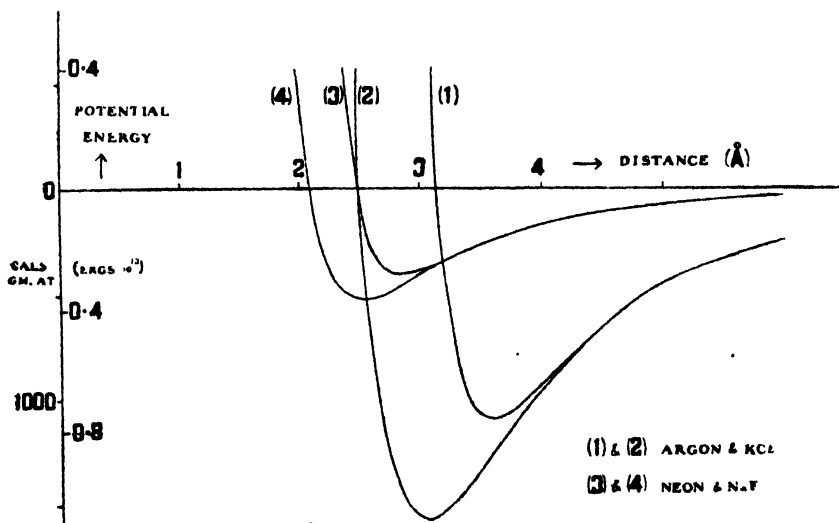


FIG. 2.—The potential energy of an argon atom outside a (1, 0, 0) plane of a KCl crystal (1) above a lattice point, (2) above the midpoint of a lattice cell. (The lattice constant $a = 6.28$ Å). Curves 3 and 4 are similar results for neon above NaF. ($a = 4.68$.)

For a rigorous determination of the heat of adsorption it would be necessary to consider the change of kinetic energy as well as potential energy on desorption. The adsorbed molecules may vibrate both normally and laterally, and may in some cases move about the surface as in a two-dimensional gas. This possibility will be considered in a later paragraph.²⁰ The vibration frequency of an argon atom normal to the surface about its equilibrium distance is found to be of the order of 10^{12} sec.⁻¹. One quantum of vibrational energy is therefore $6.5 \cdot 10^{-15}$ ergs (or about 100 cal./gram atom).²¹

¹⁹ For $n = 10$ and 11 , the corresponding values are 1500 and 1500 cal./gram atom, and 3.27 Å and 3.14 Å.

²⁰ Diatomic molecules will in general also have rotational energy in the adsorbed state, for it is known from Raman spectra that many molecules rotate even in the solid state, and rotation is not likely to be less in a state of loose Van der Waals' adsorption. But rotational energy is not likely to be affected by the forces of adsorption, and consequently its average in the adsorbed and desorbed states is probably the same. If so, the fact of rotation will not alter the energy of desorption.

²¹ The author gladly acknowledges his thanks to Miss M. J. Littleton, Wills Physical Laboratory, Bristol, for carrying out the numerical calculations of this paragraph.

§ 3. "Activated" Adsorption.

A series of interesting experiments have recently been carried out in order to determine the relation between the amount of gas adsorbed and the temperature. Benton and White²² found that hydrogen was strongly adsorbed by nickel at very low temperatures of the order of -200°C . but, on raising the temperature, the adsorption diminished to a minimum at about -180°C ., then rose to a maximum again at about -100°C ., thereafter falling steadily with rise of temperature. Similar results have been obtained by Taylor and Williamson²³ and also by Taylor and McKinney.²⁴ The heats of adsorption at the very low temperatures are of the order of 1000-2000 cal./mol., and may safely be attributed to the Van der Waals' forces discussed in the preceding paragraph. The heats of adsorption at high temperatures are about ten times as great, in some cases being as much as 30,000 cal./mol. or more.

It is almost certain that there is a change in the nature of the adsorption at the higher temperatures. The isobars of Benton and White must be regarded as the superposition of two curves, one representing the adsorption due to van der Waals' forces, the other that due to other forces whose nature has not yet been explained. The second curve then begins with little or no adsorption at temperatures below -200°C ., rises to a maximum and then falls slowly with temperature. Seeing that the heat of adsorption is greater than that of the van der Waals' type, an explanation is required as to why the adsorption is small at very low temperatures. H. S. Taylor refers to this type as "activated" adsorption, but its nature is left unspecified. Benton and White on the other hand describe it as chemisorption. They suggest that the nickel surface at the higher temperatures is covered with activated hydrogen, probably atomic, held by chemical forces. But two problems remain unsolved, *viz.* (i) why has the isobar of this type of adsorption a maximum? and (ii) what is the nature of the adsorption force?

As a basis for discussion at this meeting, I make the following tentative suggestions. The interaction between a *molecule* and a metal is of the type discussed in the preceding paragraph and is represented by curve (1) in Fig. 3. There is a small minimum at a large distance from the metal. Suppose next that the cohesion between the individual atoms and the metal is greater than the dissociation energy of the molecule. Then the energy curve of two widely separated atoms is of the type (2), with a minimum at L , the difference between the two curves at an infinite distance from the metal being the dissociation energy of the molecule. Let the two curves cross at K . Then at K no work is required to dissociate the molecule in a direction parallel to the surface. The two curves²⁵ are really two of the molecular levels of the huge molecular system M (metal) + A (atom) + B (atom), and we may now consider a process which is the reverse of predissociation—a phenomenon so often observed in molecular spectra, *viz.*, a molecule may approach the metal and remain as a molecule until it reaches the point K , then it may dissociate and switch to curve (2).*

²² Benton and White, *J.A.C.S.*, **52**, 2325, 1930.

²³ Taylor and Williamson, *J.A.C.S.*, **53**, 2168, 1931.

²⁴ Taylor and McKinney, *J.A.C.S.*, **53**, 3604, 1931.

²⁵ There must be a number of other curves between (1) and (2) corresponding to the states of rotation and vibration of the molecule at infinity. These must be considered in detail in a quantitative theory.

* See, however, the appendix at end of paper.

For a radiationless transition of this character, certain conditions are necessary. There must be no change of total angular momentum, nor a change in the total spin vector, nor a change in the parity of the molecular term. For a molecule initially in a Σ state, these conditions will usually be satisfied. A hydrogen molecule, for instance, will dissociate at K into two atoms with opposite spins, and the parity of the states before and after the transition will be even.

A molecule approaching the metal with an energy W , insufficient to reach K , might, according to quantum mechanics, penetrate the barrier, but the probability is small unless W is very nearly of the same height as the point of intersection K . The height of K above the zero energy is in fact the "energy of activation" (P) necessary for a transition from the state (1) to the state (2). If the energy of the impinging molecule is large, the molecule will swing past K at considerable speed and the probability of a switch is again small. For the best chance of a transfer

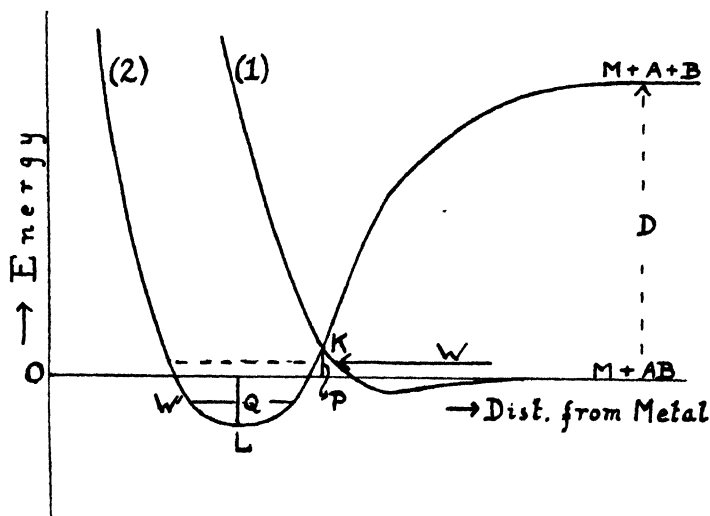


FIG. 3.—The interaction of a molecule and a metal.

the energy of the molecule must be equal to the energy of activation. It follows that both at low and at high temperatures, the probability of adsorption as atoms is small.

When this switch occurs the atoms A and B will both rush towards the solid along potential fields whose sum is given by curve (2) in the figure. They may then give up energy to the solid, and be trapped about the new equilibrium position L .

The most probable energy of translation of molecules perpendicular to the surface at a temperature T is $\frac{1}{2}kT$, and so we may expect the most favourable conditions for adsorption as atoms when $T = 2P/k$. This will not necessarily be the same as the temperature of the maximum on the isobar. The kinetics of both adsorption and desorption must be worked out in detail before this maximum can be related to the energy of activation.

The heat of adsorption observed will be the difference between the energy of the molecule before and after adsorption and therefore equal to $Q + W - W'$, where Q is the depth of the minimum L between the

zero line, and W' is the sum of the vibrational energies of the two atoms after adsorption. In the case of hydrogen adsorbed on copper, the value of Q is of the order of 10,000 to 20,000 cal./mol., so that the energy of binding, which is equal to $D + Q$, is of the order of 110,000 to 120,000 cal./mol. The energy of adsorption of each atom must therefore be of the order of 60,000 cal./gram atom for this picture to be a reasonable one. We must therefore next consider what is likely to be the nature of the cohesion between each atom and the metal.

The application of quantum mechanics to the problems presented by metals has profoundly altered our conception of the nature of a metal, and has thrown a flood of light on the phenomena of metallic conduction, electron emission, and so on. There can now be no reasonable doubt that the new theories give a more accurate picture of the nature of a metal than the free electron theories of Drude and Lorentz.

The first step was taken by Sommerfeld who supposed that the valency electrons of the metallic atoms behaved very much like an electron gas obeying the Fermi-Dirac statistics instead of the classical statistics. This view was extended by Bloch, who showed that *all* the electrons of a metal may be regarded as free and may move from end to end of a perfect lattice without resistance. On this view it is the disturbance of the perfect lattice system by thermal vibrations that causes resistance to electrical conduction. The electrons may be regarded as jumping from atom to atom and pausing for a time at each. They may thus for some purposes be regarded as bound and for others as free. There are for a metal, as for an atom or molecule a series of states or levels to which the electrons are to be allotted according to the Pauli exclusion principle.

The innermost levels arise from the $1s$ states of the separated atoms and form a band of N allowed energies, where N is the total number of atoms. To each of these, two electrons may be allotted, one of each kind of spin, so that there are $2N$ electrons in the band altogether. These correspond to the $2N$ electrons in K levels of the separated atoms. They constitute a closed group and their net conduction is zero because as many travel in one direction as in a reverse direction. To get conduction some of the electrons must reverse their direction under the influence of the applied field, and this may not be possible owing to the Pauli principle without a transition to a higher band of levels. There exist other higher closed groups of electron levels above these and then finally the uppermost electrons which can easily make transitions to other empty levels. These are the ones which contribute to electrical conduction.

These conditions apply only as long as a metal is perfect but local irregularities may introduce new levels, with wave functions localised about the irregularity. Electrons may under these conditions be regarded as localised. Skinner²⁶ has recently shown that the ejection of an electron from the lowest group of electrons causes an increase in the effective charge of one nucleus and this leads to a new set of local energy levels.

We may expect similar conditions to hold at the surface of a metal when atoms approach the surface. These are in the nature of impurities and affect the periodicity of the field near the boundary. The

²⁶ Skinner, *Nature*, 128, 114, 1931.

potential field in which the outer (or conduction) electrons of the metal move is represented diagrammatically in Figs. 4 (a) and 4 (b).

The periodic field in the metal fluctuates about a mean value of $-W$, and the surface is represented by the abrupt change in potential.

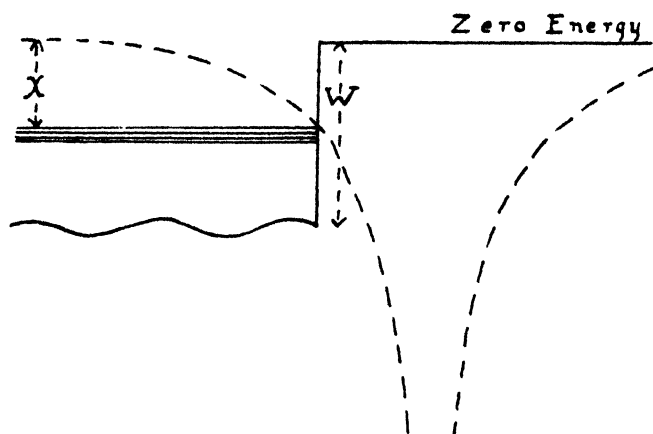


FIG. 4 (a).—The diagrammatic representation of the potential field of the conduction electrons of a metal. (The dotted curve gives a similar representation of the potential field of a H nucleus on one electron.)

There are a series of levels in this field, the lowest of which corresponds to zero kinetic energy, and there are others of gradually increasing kinetic energy. The electrons with the greatest kinetic energy are still

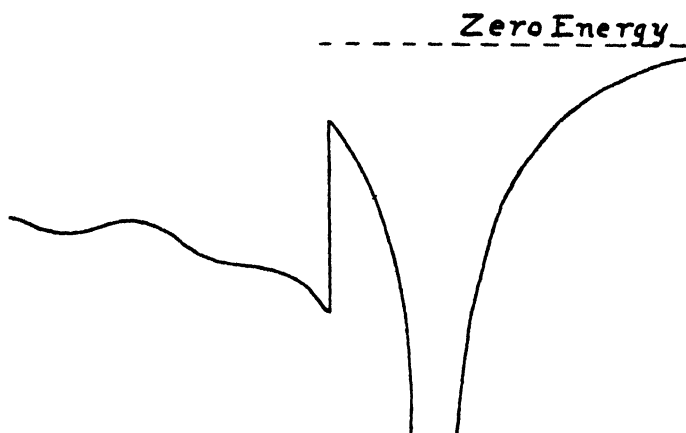


FIG. 4 (b).—The potential energy near the surface of a metal when a hydrogen nucleus is present.

χ units below the zero level, and this energy must be supplied to lift them from the metal. This is usually associated with the work function.

The actual potential energy in the presence of another atom will consist of the algebraic sum of the potential energies at any point and may be represented by Fig. 4 (b) or diagrammatically by Fig. 5.

There is a local dip in the potential energy at the surface represented

by B and a region of low potential energy outside represented by A .²⁷ There will in consequence be local energy levels near the surface. The lowest level may be in region A as shown, and the second in region B . The wave functions appropriate to these levels are localised and are the dotted curves shown in the figure. They may overlap and then the exchange phenomenon may occur when electrons are allotted separately to them. This will cause a lowering of the total energy of the two electrons (as occurs in the homopolar bond) and give cohesion. The wave functions of the other levels will extend throughout the metal but will show slight changes of character above the region B . The adsorption bond may be regarded as due to the interaction of the valency electron of the approaching atom with one of the conduction electrons of the metal. The two together form a closed shell.

In some cases the adsorbed atom may give up its electron to the metal. This is known to occur when the energy of the electrons in the metal is lower than that of the electron in the atom, as for example

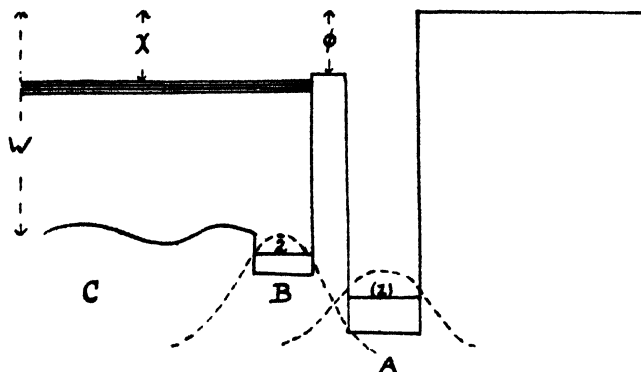


FIG. 5.—The diagrammatic representation of the potential field on one electron at the surface of a metal in presence of another atom.

in the case of caesium on tungsten. Such a process is really very similar in character to the transfer of an electron from one atom to another in ionic cohesion (such as NaCl). The adsorbed ion must then be held to the surface by electrostatic forces, but these forces must cause a change in the potential field near the surface.

At higher temperatures some of the electrons of the lower bands of levels in the metal, to which reference was made earlier, may be promoted to the upper conduction level. Interaction may then occur between electrons in the lower band (now incomplete) and an outer atom. We should then have to add to Fig. 3 another level due to an excited metal + two normal atoms, and this might lead to a minimum lower than L , though the heat of activation for adsorption would at the same time be raised. Adsorption of this kind would be analogous to the interaction of two atoms to form a molecule when one of the electrons of an inner core of one of them is transferred to a higher level (as for example when one of the $3d$ electrons of copper is promoted to a $4s$ state

²⁷ We note in passing that there is a diminution in the potential barrier at the surface (indicated by ϕ), and if other atoms approach the surface to cause a lowering of the potential beyond A , there may be a large increase in the electrical emission of the solid. Such changes due to surface layers have indeed been observed.

to combine with hydrogen to form CuH). Now Garner²⁸ has observed such a change in the process of adsorption at high temperatures in the case of hydrogen and carbon. Adsorption of this kind is found to be irreversible in that one of the surface atoms of the solid is torn away during desorption. This means that the cohesion between the adsorbed atom and a metal atom is stronger than that between the metal atoms themselves. There are thus various types of adsorption just as there are various types of bonds in molecules, of which the ionic or polar represents one extreme case, the homopolar another.

If atoms were adsorbed on a surface in the way here suggested, *viz.*, according to Fig. 3, and the temperature were suddenly lowered, the atoms would not be desorbed but would remain attached to the solid vibrating about their equilibrium positions. At very low temperatures *molecules* could be adsorbed in a layer above them by the long range van der Waals' forces, as is clear from Fig. 3, where the minimum of curve (1) is well beyond that of curve (2). This suggests that an isobar which is obtained on a rising temperature will not be reproduced on a falling temperature. The minimum of the isobar may disappear. Benton and White²² found that when nickel which had sorbed its full amount of hydrogen at 0° C. was cooled to -186° C., it adsorbed as much more as if the surface had been initially free of gas.

A further possible result of the energy diagram may be inferred. A molecule adsorbed by van der Waals' forces at low temperatures will normally vibrate about its minimum (curve 1, Fig. 3), but there is always a finite though small probability that it will penetrate the barrier to curve (2). There may thus be a slow change from van der Waals' adsorption to activated (or dissociated) adsorption even at low temperatures.

§ 4. Slow Sorption Due to Diffusion.

It was first shown by McBain²⁹ that solids can take up gases in many ways other than by causing them to adhere to the outer surface, and he introduced the general term "sorption" to include all such processes. This phenomenon has since been confirmed by many other workers, and there is now considerable material about *adsorption* on the outer surface and *absorption* within the body of the solid. In some very careful experiments Ward has recently succeeded in separating the two processes of adsorption and absorption. When hydrogen at a known pressure is allowed to come in contact with freshly prepared copper there is an immediate fall of pressure, followed by a further slow decrease of pressure. At room temperatures the copper may take up gas for several months. The first sudden drop of pressure is attributed to adsorption, because the process seems to be reversible. When the pressure of the outside gas is reduced, there is immediate desorption. Owing to the great difference of speed between adsorption and absorption, it was possible to examine the two separately in detail. In this paragraph we shall be concerned only with the second slow process.

Ward's experiments were carried out at temperatures varying from 25° C. to 200° C. and his results may be summarised as follows:—

(i) for a given temperature and pressure, the amount of gas absorbed is proportional to the square root of the time;

²⁸ Garner and Kingman, *Nature*, **126**, 352, 1930; *Trans. Far. Soc.*, **27**, 322, 1931.

²⁹ McBain, *Phil. Mag.*, **18**, 916, 1909.

(ii) for a given temperature, the amount absorbed divided by the square root of the time is proportional to the concentration on the outer surface;

(iii) the process of absorption depends on temperature according to an exponential factor $e^{-E/kT}$, where E is a constant, *viz.*, an activation energy.

Ward suggests, in explanation of his results, that the gas diffuses into the interior of the copper forming a solution; at the same time he postulates that the hydrogen is adsorbed as molecules. He is not, however, able to suggest an explanation of the energy of activation, which he determines to be 14,100 cal. per gram-molecule.

In the preceding paragraph we have suggested an interpretation of adsorption between an atom and a metal, but in doing so we neglected the fact that a metal is crystalline in form. The surface of a metal must be periodic in structure and the conditions must be different above different points of metallic lattice. We have already noted in § 2 such a variation of the field outside a solid. The potential energy field outside a surface,

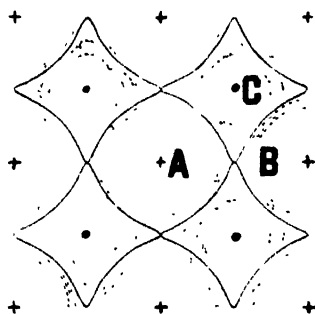


FIG. 6.—The potential field in a plane parallel to a surface.

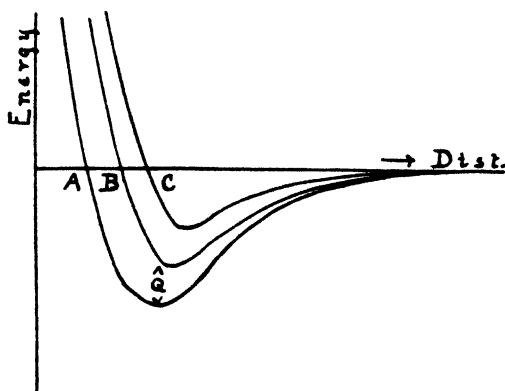


FIG. 7.—The potential field normal to a surface.

whose unit surface cell is a square, may therefore be expected to have the form shown in Fig. 6. This picture of the field applies, of course, only when the surface atoms are at rest. Thermal agitation will cause rapid fluctuations of this field, but the diagram given may well represent the mean field even at normal temperatures. The crosses in the figure represent the positions of the minima and the dots the maxima. The continuous line is an equipotential line extending throughout the surface.

For a complete picture of the potential field, we require as well a series of diagrams showing the variation of potential as a function of the distance from the surface. In Fig. 7 we show three such figures corresponding to the points *A*, *B* and *C* of the surface potential energy diagram.

An adsorbed atom will normally vibrate about the positions of minimum potential energy, and the vibration may be lateral or normal, or both together. If, however, it receives from the solid enough energy to reach the continuous equipotential line, it may travel along the surface until it loses energy by colliding with another adsorbed atom or by interaction with the solid.

According to quantum mechanics it is possible for a particle vibrating about a position A to penetrate the potential barrier separating it from the next minimum, but a rough calculation shows that the probability of doing so is extremely small except when the energy of vibration is nearly sufficient to take it to the continuous equipotential line.³⁰

We may thus distinguish between two states of adsorbed atoms, a *vibrating* state and a *mobile* state. These are closely analogous to the solid and liquid states of three dimensional fluids, and it is tempting to classify the possible states of the adsorbed gas as solid, liquid and gaseous, but the use of such terms would probably lead to confusion.³¹

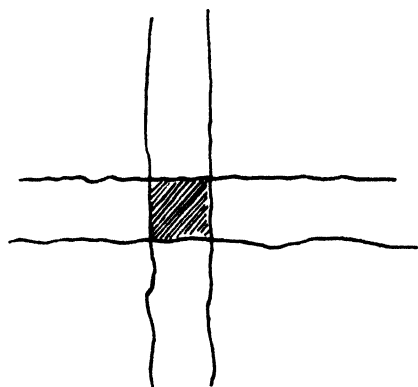


FIG. 8.—Diagrammatic representation of "outer" and "inner" surfaces of a solid.

Now it is generally accepted that the outer surface which a solid presents to a gas is not by any means the whole of its surface area. Even perfect crystals develop cracks as a result of unbalanced forces at the surface. Lennard-Jones and Dent³² showed that a two-dimensional layer of a crystal of the sodium chloride type would have a spacing about 5 per cent. less than that of the solid crystal. There must therefore be a lateral tension tending to produce lateral contraction, and it is likely that this tension is relieved by small innumerable cracks spreading over the whole surface.

In Fig. 8 is shown a diagrammatic representation of a portion of the surface. The shaded area is the portion of the outer area, bounded on each side by a deep crevasse. The latter are probably deep and narrow and almost completely protected from bombardment by the molecules of the gas. On the diagram the area of the walls of the cracks are straightened out for purposes of illustration. Although protected from direct bombardment, these inner areas may be reached by lateral diffusion from the outer surface.

Only those adsorbed atoms in the mobile or "activated" state can diffuse from the outer to the inner area. We now consider in some detail this process of diffusion. Suppose that each atom is activated to the mobile state γ times per second, so that $\gamma n dx dy$ is the number of atoms which leave an area $dx dy$ in unit time, n being the concentration of adsorbed atoms on the outer surface. These atoms will travel an average distance l before deactivation—analogueous to the free path of atoms in a gas. The probability that an atom will travel a distance equal to or greater than r is then $e^{-r/l}$.

We concentrate attention on the atoms crossing an element $d\sigma$ of any prescribed boundary. Let $dx dy$ be an element of area distant r

³⁰ The time required for a hydrogen atom to cross a potential barrier of height 10,000 cal. and thickness 1 Å is about 10^{10} secs.; that to cross one of height 1000 cal. and thickness 0.5 Å is about 100 secs.

³¹ This picture suggests that the process of melting of a solid consists in a transition of surface atoms from the vibrating to the mobile state. See note A at the end of the paper.

³² Lennard-Jones and Dent, *Proc. Roy. Soc.*, **121A**, 247, 1928; cf. also Smekel, *Physik. Z.*, **26**, 707, 1925; *Z. Physik*, **48**, 869, 1927; Zwicky, *Proc. Nat. Acad. Sc.*, **15**, 253, 1929; Stranski, *Z. Elektrochemie*, **36**, 25, 1930; for a discussion of cracks.

from $d\sigma$ and situated in a direction making an angle θ with its normal. Then the number of the atoms which are activated in $dx dy$ in unit time and cross $d\sigma$ is given by

$$\gamma n e^{-r/l} \left(\frac{\cos \theta d\sigma}{2\pi r} \right) dx dy,$$

since $d\sigma \cos \theta / 2\pi r$ is the fraction of atoms which travel in the direction of $d\sigma$. If there is a uniform gradient in the concentration in a direction perpendicular to $d\sigma$ we may write

$$n = n_0 + r \cos \theta \frac{\partial n}{\partial x},$$

n_0 being the concentration at the boundary $d\sigma$. The excess of those crossing from the side of greatest concentration over those coming from the other side is

$$\int_0^\infty \int_0^{2\pi} \gamma \left(n_0 + \frac{\partial n}{\partial x} r \cos \theta \right) e^{-r/l} \frac{\cos \theta d\sigma}{2\pi r} r d\theta dr,$$

the integration being over all values of r and θ . This leads to the result that the net flow across unit length of the boundary is*

$$\frac{1}{2} \gamma l^2 \frac{\partial n}{\partial x}.$$

If we suppose the average lateral velocity of the atoms to be \bar{c} and the time during which they remain mobile to be τ , then $l = \bar{c}\tau$. Further γ , being the number of times a single atom is activated per second, is equal to the reciprocal of the interval of time between two successive activations of the same atom. Let this time be τ^* , then we have for the net flow

$$\Gamma = - \frac{\bar{c}^2 \tau^2}{2\tau^*} \frac{\partial n}{\partial x},$$

the negative sign indicating flow in a direction opposite to that of increasing concentration.

If we consider the numbers entering and leaving an area included between two parallel boundaries distant dx apart, we immediately find

$$\frac{\partial n}{\partial t} = - \frac{\partial \Gamma}{\partial x} = D \frac{\partial^2 n}{\partial x^2},$$

where

$$D = \bar{c}^2 \tau^2 / 2\tau^*.$$

This equation, which is an ordinary diffusion equation, determines the flow from the outer surfaces along the cracks to the inner surface. The concentration of adsorbed atoms at the outer surface will be kept at a constant value by the bombarding gas, provided the amount of the latter is large compared with the amount adsorbed.

If the cracks are very deep, then initially the solution of the equation is

$$n = n_0 \left\{ 1 - \frac{2}{\sqrt{\pi}} \int_0^{\xi} e^{-t^2} dt \right\},$$

where

$$\xi = x / 2\sqrt{Dt}.$$

This solution is accurate for infinitely long cracks, when the concentration at one end is kept constant and that at the other is zero initially.†

* If all the atoms are assumed to travel the same distance l when activated, the corresponding result is $\frac{1}{2} \gamma l^2 \partial n / \partial x$.

† See Note B below.

The net number flowing at any time from the outer patch of surface to the inner surface per unit length of its perimeter is

$$(\Gamma)_{x=0} = -D \left(\frac{\partial n}{\partial x} \right)_{x=0} = n_0 \sqrt{\frac{D}{\pi t}}.$$

Hence the total amount in the interior of the solid per unit length of boundary of an outer patch of surface is

$$\begin{aligned} S &= \int_0^t (\Gamma)_{x=0} dt = 2n_0 \sqrt{\frac{Dt}{\pi}} \\ &= n_0 \bar{c} \tau \sqrt{2t/\pi \tau^*}, \end{aligned}$$

and is therefore proportional to the square root of the time as observed by Ward.[§]

Deactivation of a mobile atom may occur as a result of (i) a collision with another mobile atom, (ii) a collision with a vibrating adsorbed atom, and (iii) interaction with a vibrating atom of the solid. If the energy of activation E is small compared with kT , then most of the atoms will be in the mobile state and events of type (i) will be numerous compared with those of type (ii). The atoms will then behave very much like a two-dimensional gas.

If, however, $E \gg kT$, events of type (i) will be comparatively rare. The relative importance of (ii) and (iii) will depend on the amount adsorbed. If the concentration of adsorbed atoms is small compared with the concentration of surface atoms of the solid (and therefore small compared with the saturation value of the concentration in a monomolecular layer), then interaction with the solid may be expected to play the predominant part in terminating the "free path." In this case the solid is responsible both for activation and deactivation. Under these conditions the atoms will probably move along the surface very much like projectiles in a gravitational field. The "time of flight" will then be of the order of the period of vibration of the atoms normal to the surface, viz., 10^{-13} secs.

It can easily be shown that the fraction of atoms with an energy E_0 or over is $e^{-E_0/kT}$. It follows that the ratio of the time, during which any one atom is activated, to the time, during which it is not activated, is $e^{-E_0/kT}$. Hence we may substitute for τ and τ^* the values

$$\tau = \tau_0, \quad \tau^* = \tau_0 e^{E_0/kT}$$

where τ_0 is the period of vibration of an adsorbed atom normal to the surface.

Finally if Λ is the total perimeter of all the patches of surface which are exposed to the bombardment of the gas, we have for the total amount of gas "inside" the solid after time t ,

$$S = \Lambda n_0 \bar{c} e^{-E_0/2kT} \sqrt{2\tau_0 t/\pi}.$$

In this formula \bar{c} is the average velocity of the mobile atoms *parallel to the surface*. Assuming a Maxwellian distribution of velocities, the fraction of atoms with velocity components between u and $u + du$, v and $v + dv$ is

$$f(u, v) du dv = \frac{m}{2\pi kT} e^{-m(u^2 + v^2)/2kT} du dv.$$

§ See Note C, below.

The fraction with an energy greater than $E_0 (= \frac{1}{2}mc_0^2)$ is then

$$\int_{c_0}^{\infty} f(u, v) 2\pi c dc = e^{-mc_0^2/2kT} = e^{-E_0/kT},$$

and the average velocity is

$$\begin{aligned}\bar{c} &= \int_c^{\infty} f(u, v) c^2 dc \div \int_c^{\infty} f(u, v) c dc \\ &= c_0 + (\pi kT/2m)^{\frac{1}{2}} e^{mc_0^2/2kT} \operatorname{erf}(c_0 \sqrt{m/2kT}),\end{aligned}$$

where $\operatorname{erf}(x)$ is the error function defined by

$$\operatorname{erf}(x) = \frac{2}{\sqrt{\pi}} \int_x^{\infty} e^{-x^2} dx.$$

When $E_0 (= \frac{1}{2}mc_0^2)$ is large compared with kT , the second part of the expression for \bar{c} is vanishingly small and we have approximately

$$\bar{c} = c_0.$$

As a further refinement we should consider the fluctuation in the lateral velocity of an atom during its "flight" owing to the changing potential of the field parallel to the surface. When an atom has just sufficient energy to become mobile, its velocity at the top of a col (point *B* in Fig. 6) is zero, but it rapidly accelerates towards a minimum *A* and then diminishes again. The motion is then very similar in type to that of a simple harmonic oscillator and the average kinetic energy is equal approximately to the average potential energy and therefore to the critical energy E_0 .

We may therefore write for the amount of gas *adsorbed*

$$S = \Lambda n_0 c_0 e^{-E_0/2kT} \sqrt{2\tau_0/\pi},$$

and for ease of reference, we recall the meaning of the symbols: Λ is the total boundary of all the areas of outer surface, n_0 is the total concentration of *adsorbed* atoms on the outer surface, E_0 is the energy required for an atom to become mobile and equals $\frac{1}{2}mc_0^2$, τ_0 is the period of vibration of an adsorbed atom normal to the surface and t is the time at which S is measured, assuming $S = 0$ when $t = 0$.

The concentration n_0 depends on the pressure and temperature of the gas. For a given pressure and temperature, the formula shows that S is proportional to the square root of the time. This is in agreement with the observations of Ward.⁵ His results are shown in Fig. 9.

Again $S/n_0\sqrt{t}$ is independent of pressure and so should be constant for a given temperature. This also is a result observed by Ward.

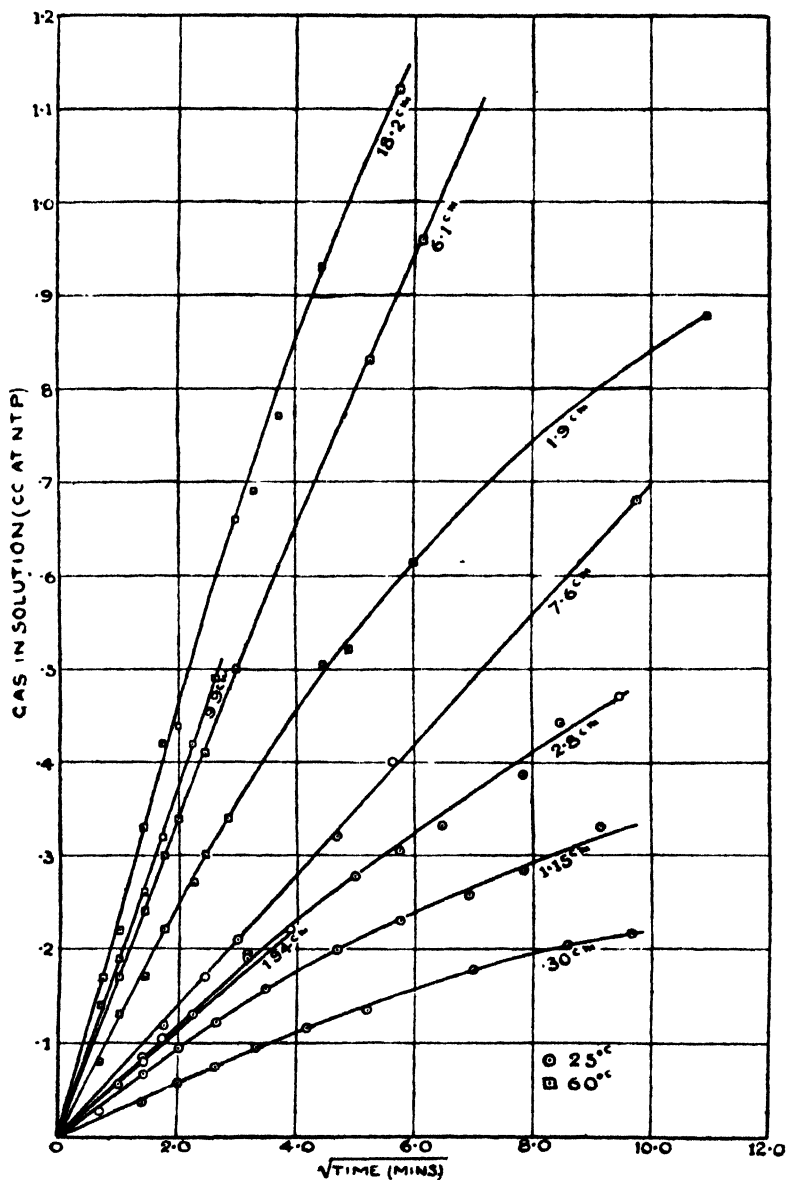
Finally Ward plots $\log_{10} S^2/q^2t$ against $1/T$ where q is the total amount on the outer surface, and his results are reproduced in Fig. 10.

From the above formula for S , substituting $q = n_0\Delta$, where Δ is the total area of the outer surface, we find

$$\log_{10} \frac{S^2}{q^2t} = \log_{10} \frac{2\Lambda^2 c_0^2 \tau_0}{\pi \Delta^2} - \frac{E_0}{kT \log_e 10}$$

so that the slope of Fig. 10 is proportional to E_0 . The value of E_0 thus determined for hydrogen on copper is 14,100 cal. per gram atom. The

picture of diffusion here suggested gives a simple explanation of this "heat of activation."



[From Ward, *Proc. Roy. Soc.*, Vol. 133, p. 525, Fig 1.]

FIG. 9.—The amount of hydrogen absorbed by copper as a function of the time (Ward).

Suppose that the "constant" of the straight line relation between $\log_{10} S^2/q^2t$ and $1/T$ is a , then

$$\frac{2\Delta^2 c_0^2 \tau_0}{\pi \Delta^2} = 10^a.$$

If each patch of the outer surface were a square of side d , the number of patches would be Δ/d^2 and the total perimeter $\Lambda = 4d \cdot \Delta/d^2 = 4\Delta/d$. The side of each patch would then have a length given by

$$d = \{32c_0^2\tau_0/\pi 10^a\}^{\frac{1}{2}}.$$

The value of a for Ward's figure is approximately 8.3.* Now c_0 is the velocity of a hydrogen atom appropriate to an energy of 14,100 cal. per gram atom and is therefore of the order of 10^6 cms./sec., while τ_0 is of the order of 10^{-13} to 10^{-14} secs. It follows that d is of the order of 2 to 6 $\cdot 10^{-4}$ cms.—a rough but reasonable estimate of the average size of a patch on a surface.†

The figures obtained for E_0 and c_0 for this particular case permit of a calculation of the order of magnitude of certain other quantities relating to the mobility of atoms on a surface. If τ_0 is of the order of 10^{-13} secs., and c_0 of the order of 10^6 cms./sec., then the "free path" is of the order of 10^{-7} cms. The duration of time between successive activations of the same atom is of the order of $\tau_0 e^{E_0/RT}$ and, when $E_0 = 14,000$ cal. and $T = 350^\circ$ absolute, this is about 10^{-4} secs. The total possible forward movement of any atom per second under these conditions is

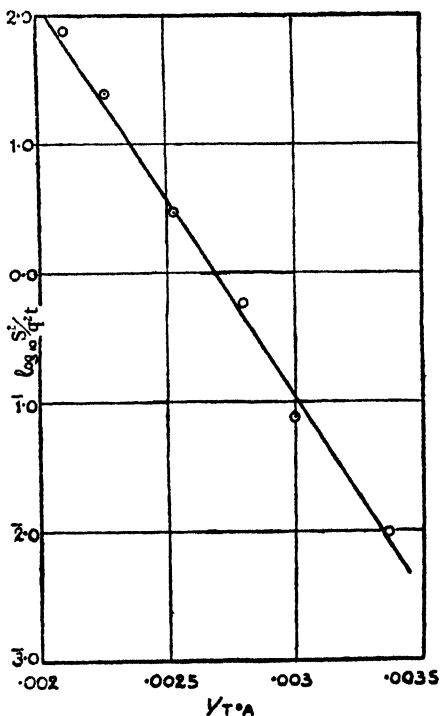
$$10^{-7} \div 10^{-4} \text{ cms.} = 10^{-3} \text{ cms.},$$

but, as shown in Note E, below, the average distance travelled in one second is 10^{-5} cms.

It may at first sight appear strange that the heat of activation should be 14,100 cal. per gram atom and therefore 28,200 cal. per gram molecule, when the observed heat of adsorption is less than this quantity. This can be explained in terms of the picture suggested in the preceding paragraph. The heat of adsorption which is observed refers to the molecule and is therefore about 100,000 cal. less than the heat of adsorption of two separate hydrogen atoms. The true heat of adsorption of each atom must be of the order of 60,000 cal./gram atom.

* Ward, however, measures time in minutes so that the value of a to be used in the theoretical formula is $(8.3) \div \log_{10} 60$.

† See Note D, below.



[From Ward, *Proc. Roy. Soc., A*, Vol. 133, p. 530, Fig. 5, 1931.]

FIG. 10.

For each type of adsorption there will be a characteristic energy of activation before diffusion can take place. Even for van der Waals' fields there will be a small and definite variation in the potential field parallel to the surface. In § 2 we have calculated the magnitude of the variation for the case of argon over a KCl crystal. The energy of activation for this case is of the order of 250 cal./gram atom.³³

Lateral diffusion for a given pressure is determined mainly by the term $e^{-E_0/kT}$ and will be large when $kT \gg E_0$ and small when $kT \ll E_0$. The transition temperature defined by $kT_0 = E_0$ is, in this case, 125° abs. Bawn³⁴ found that CO was adsorbed in mica almost instantaneously at 195° abs., whereas at 90° abs. sorption was not complete until after forty-five minutes. This suggests that at the higher temperature the process consisted of both *adsorption* and *absorption*, and that the latter was rapid, whereas at the low temperature *absorption* or diffusion was slow. Benton and White³⁵ found a similar slow adsorption at very low temperatures and an instantaneous one at higher temperatures. In this connection, too, it is of interest to note that Davisson and Germer³⁶ found that gas adsorbed on nickel exhibits a definite spacing at room temperature, but not at a temperature of 150° C.

When a new type of adsorption begins such as that described in § 3, both the heat of adsorption and the heat of activation necessary for migration increase considerably in magnitude. There will again be a critical temperature for the diffusion process, and diffusion for the new type of adsorption may be slow even when, at the same temperature, that due to van der Waals' attraction is large. It is incorrect therefore to argue, as has often been done, that because diffusion is rapid at temperatures of the order of 200° abs. it must be instantaneous at all higher temperatures.

Notes (added in proof).

Note A.—The process of migration suggested in § 4 may be the first stage in the melting of a solid. If a solid consists, as has often been suggested, of small blocks of the order of 10^{-4} cms. or less, a rapid migration of atoms around their surfaces may cause them to float away from one another. There is evidence of the appearance of such small blocks during melting.

Atoms, which are in positions of high potential energy such as edges and corners at low temperatures, will tend to migrate to positions of lower potential energy when the temperature is raised. The corners of some metals may, for instance, tend to become rounded considerably below the melting-point of the solid owing to the slow migration of the atoms.

Note B.—The solution of the diffusion equation given in the text applies to the case when the concentration of atoms inside the solid initially is zero. If there is a uniform concentration n_i along the crack at $t = 0$, the solution of the equation is

$$n = (n_0 - n_i) \left\{ 1 - (2/\sqrt{\pi}) \int_0^{\xi} e^{-\xi^2} d\xi \right\} + n_i,$$

³³ This is the difference between the minima of curves A and B in Fig. 7. The curves given in Fig. 2 are curves A and C.

³⁴ Bawn, *J.A.C.S.*, **53**,

³⁵ Benton and White, *J.A.C.S.*, **52**, 2325, 1930.

³⁶ Davisson and Germer, *Physic. Rev. (2)*, **30**, 705, 1927; Germer, *Z. Physik*, **54**, 408, 1929.

and total amount which flows into the interior across unit length of boundary in time t is

$$S = 2(n_0 - n_i)(Dt/\pi)^{1/2}$$

Note C.—The result that the amount absorbed is proportional to the square root of the time is true only for finite values of t . When $t = 0$ the diffusion equation does not hold, because it is tacitly assumed in its derivation that $\partial n/\partial x$ is finite and continuous. Initially there is a discontinuous change from $n = n_0$ to $n = 0$ at $x = 0$. There is then migration only from one side and the number which cross an element of boundary $d\sigma$ at $x = 0$ in time δt is

$$\delta t \int_0^\infty \int_{-\pi/2}^{\pi/2} \gamma n_0 e^{-r/l} \cos \theta \, d\sigma \, d\theta \, dr / 2\pi \\ = \gamma n_0 l \, d\sigma \, dt / \pi,$$

so that initially

$$ds/dt = \gamma n_0 l / \pi,$$

and the total amount in a crack is proportional to the time.

After a very small time owing to the finite concentration of atoms beyond the boundary, atoms begin to migrate back again and the rate of diffusion is

$$ds/dt = (\gamma l / \pi)(n_0 - n),$$

where n is the concentration just beyond the boundary.

As the atoms diffuse along the crack this law merges into that given above and S increases according to the square root of time. We note that then S is proportional to n_0 multiplied by the average distance moved by an atom in time t , viz. $\delta = \sqrt{2Dt}$ (cf. note E, below).

Note D.—The value obtained for the distance between cracks suggests that the patches postulated in the above theory really correspond to the surfaces of

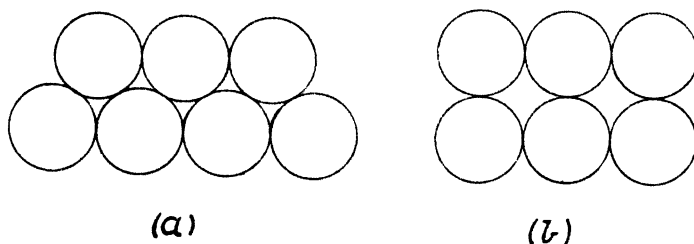


FIG. 11.

microcrystals and the cracks to gaps between loosely fitting boundaries of neighbouring microcrystals. Ward records that the copper used by him consisted of particles of an average size of $12 \cdot 10^{-4}$ cms., some of them being as small as $6 \cdot 10^{-4}$, others as large as $21 \cdot 10^{-4}$ cms. The fields of force here postulated between the atoms and the surface are short-range forces, like those of the homopolar type, and probably fall off exponentially with distance. The fields of two surfaces will not sensibly overlap unless the distance between them is less than (say) 4 or 5 Å; in fact, if two successive planes of a face-centred cubic crystal, such as metallic copper, are displaced from their normal interpenetrating positions as shown diagrammatically in Fig. 11 (a) to positions shown in Fig. 11 (b), they expose a number of tubular holes perpendicular to the plane of the paper along which a small atom such as hydrogen might easily migrate.

Note E.—The average movement of an atom is given by the formula for the Brownian movement, viz., $\delta = \sqrt{2Dt} = \sqrt{\gamma l^2 t}$. In the particular case here considered $\delta = 10^{-5} \sqrt{t}$ cms, when t is measured in seconds, so that 100 seconds are required for a movement in one direction of 10^{-4} cms.

Appendix (*added in proof*).

The process of activated adsorption (or of dissociation and adsorption) suggested in § 3 is not complete because it neglects the periodicity in the potential field parallel to the lattice structure, a feature which was found to be important in the other sections of the paper. Potential energy diagrams such as Fig. 3 are possibly only for changes of energy in one dimension. They have proved of great value in discussions of the interaction of two atoms in a molecule, but they do not lend themselves to generalisation when more than one coordinate is necessary to specify a configuration. The

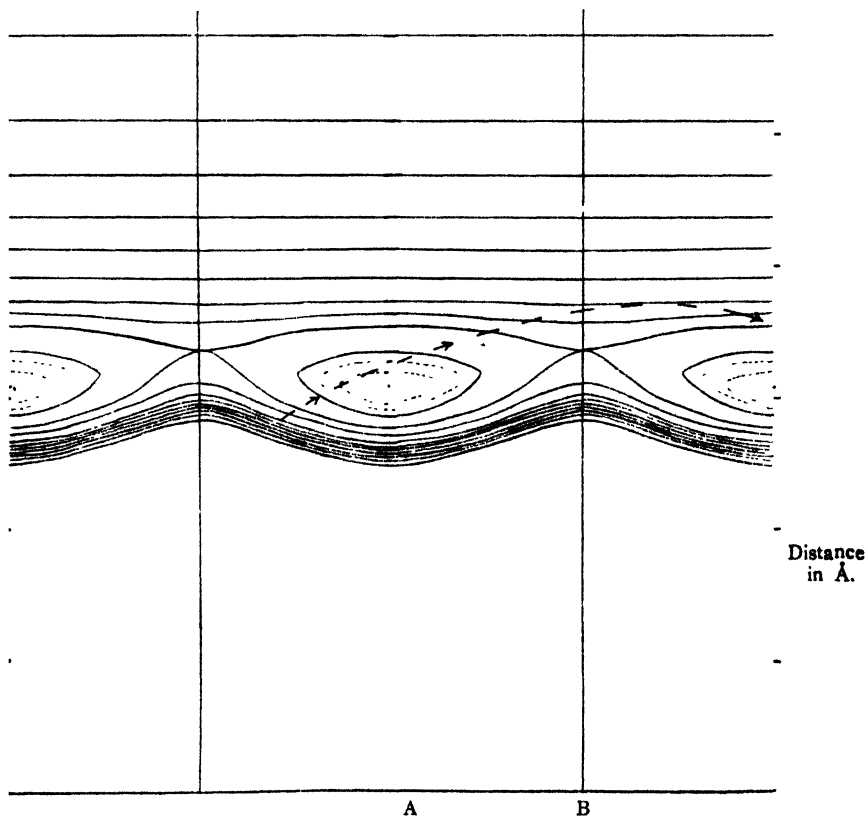


FIG. 12.—A section of the potential field of an argon atom above a 100 plane of KCl. The dotted line shows a typical path of a migrating atom.

potential field above a solid varies in three dimensions. In this case the potential field may perhaps be best represented by a system of three dimensional contours. If the same method were applied to Fig. 3, it would consist of a series of dots along the axis, placed to show equal increments of potential energy. Before considering the generalisation of the process represented by Fig. 3 it may be helpful to consider pictures of the potential field outside a solid.

First we consider the potential field due to van der Waals' forces. In Fig. 2 in the text we have given the potential energy of an argon atom above two points of a KCl crystal. A more complete representation is shown in Figs. 12 and 13. The first of these gives a section of the field by

a plane, which is perpendicular to the surface and intersects it midway between two rows of ions, while the second gives a section by the same plane and another one, which is at right angles to it and intersects the surface in a row of ions.

These figures show clearly the positions of the absolute minima of energy lying immediately above the mid-points of the lattice cells. Surrounding them are a series of closed surfaces, which prescribe the limits within which an atom may move when it has a certain total energy. An atom may vibrate anywhere within such a surface, but its mean position will, of course, be the same as that of the absolute minimum. Atoms moving thus are described in the text as *vibrating* atoms. Their motion is very much like that of an atom in a solid.

For a certain critical energy value, the potential surface round each minimum touches those of its four neighbours, and thus the composite surface extends from end to end of the crystal. An atom with this energy may migrate along the solid, but the conditions under which it may do so are sharply defined, for it can only pass from one closed surface to the next by passing through a definite point. The next potential contour resembles a series of intersecting tunnels of variable cross section. The narrowest part of the tunnel is shown in the right-hand portion of Fig. 13. As the energy increases the tunnels gradually open out until a surface is reached in which the upper and lower parts touch only at isolated points. After this the potential surfaces consist of two separated parts and resemble an underground cavern with a wave-like floor and ceiling.

This picture clarifies the process of migration proposed in § 4 of the paper. An atom with sufficient energy may follow a path like that shown by the dotted line in Fig. 12. Until it changes its energy, it cannot move out of the region prescribed by a pair of the upper and lower potential surfaces.

This picture of the potential field may be used to explain the reflection

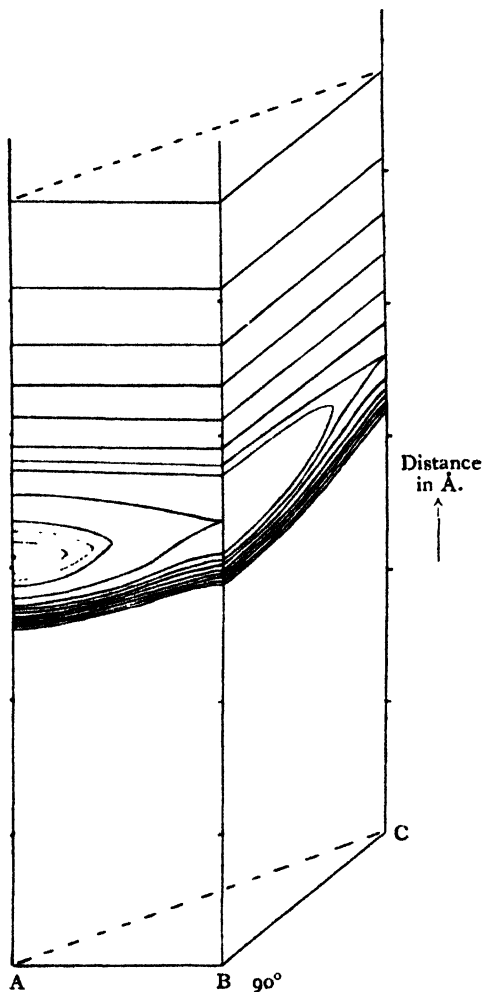


FIG. 13.—Two sections of the potential field of an argon atom above 100 plane of KCl.

phenomena obtained by Stern, Estermann and others, when a stream of inert gases impinge on a crystal of the KCl type. Such atoms move through the potential field until they meet one of the lower surfaces such as depicted in Fig. 12. The lateral periodicity of this field will affect the atoms just like a cross-ruled diffraction grating and diffraction patterns are to be expected. In deriving Fig. 12, however, the simplifying assumption has been made that the forces exerted by the chlorine and potassium ions on

argon atoms are the same. A more detailed calculation should take into account their differences and would result in wave-like surfaces with twice the period of those shown in the figure. Alternate crests would be higher than those in between them. The observed reflection patterns of Stern require such a doubling of the space lattice of the solid.

We now suppose a similar system of surfaces drawn for the van der Waals' field between a metal such as copper and a *molecule* such as hydrogen. On the same figure we superimpose another system of surfaces to represent the interaction of a hydrogen *atom* with the same surface. Owing to the small size of the atom it is able to penetrate deep into the surface at the mid-point of a lattice cell, though above a surface atom, it is held off by the large size of the metal atom. We postulate a system of surfaces, of which Fig. 14 represents a section made by a plane perpendicular to the surface and intersecting it along a diagonal of a lattice cell. From the energy values of these surfaces, we subtract half the dissociation energy of the molecule and then

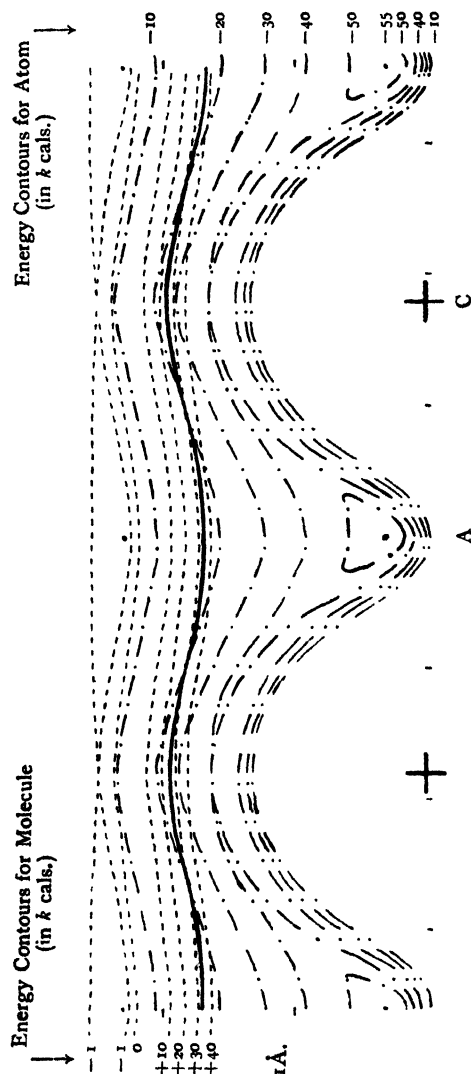


Fig. 14.—Two systems of potential surfaces and the surface of intersection.

find the points where the van der Waals' field and the atomic field have the same value. These points lie on another surface, which we may call the *surface of intersection*. This surface is the generalisation of the *point of intersection K* of the curves in Fig. 3.

If now a hydrogen molecule approaching the metal penetrates the potential field to such an extent that its nuclei simultaneously arrive at the

surface of intersection, say with one nucleus above one lattice cell and the other above the next one, then dissociation may occur without change energy. For there may then occur a double electron switch, and a bond may be formed between one hydrogen atom and one lattice cell of the metal, and another one between the other atom and the next cell.

It appears from an examination of Fig. 14 that the energy necessary for a molecule to reach the *surface of intersection* depends on the part which is approached. Some parts are more accessible than others; in other words, the energy of activation necessary for the change from molecular binding to atomic binding depends on the line of approach. In the Fig. the energy is least on the surface of intersection above C, that is above a metal atom. It suggests that there are certain optimum conditions under which dissociation occurs. Probably these conditions imply that a molecule shall arrive at the surface in such a way that its atoms are astride a projecting metal atom. The lattice spacing will determine the shape of both the molecular and the atomic potential surfaces and therefore also the surface of intersection. There may be an optimum lattice spacing for which the energy of activation for dissociation is a minimum.

We may anticipate a similar process in desorption. It is not necessary that atoms shall be ejected from a surface completely before they recombine to form molecules. If two atoms receive enough energy from the metal to reach the *surface of intersection* simultaneously from neighbouring cells, they may recombine and be desorbed as a molecule.

A similar process may be pictured between dissimilar atoms. If atoms of two types A and B are adsorbed, there will be characteristic potential surfaces for each and molecular potential surfaces for the molecules A_2 , B_2 and AB. There will likewise be various *surfaces of intersection*, and recombinations may occur in the way described above, leading to desorption as A_2 , B_2 or AB. Such a process may well be an important factor in Catalysis.

*Wills Physics Laboratory,
The University, Bristol.*

THE MIGRATION OF ADSORBED MOLECULES ON SURFACES OF SOLIDS.

By M. VOLMER.

Received 7th December, 1931.

The general thermodynamic theory of adsorption given by Gibbs knows of no fundamental difference between the surfaces of solids and liquids. Accordingly, this theory makes no distinction with respect to the change of the surface tension brought about by adsorbed molecules. The analogy existing between solid and liquid solutions in respect of the laws of osmosis, which contains the assumption of a diffusion, be it ever so slow, in the solid phase, should have suggested the idea of looking for a migration of adsorbed substances on the surface. It is significant, however, that this phenomenon was not discovered in that way. The discovery was rather the result of an accidental observation. Even more striking is the fact that after the publication

of the experiments the reality, even the possibility, of establishing such a surface migration met with doubts on many sides. Meantime, however, a number of observers established the existence of this phenomenon on various occasions. All doubts, therefore, have vanished, and one has already come to consider the process as a self-evident consequence of the kinetic theory. In the following I shall try to give a survey of the relevant facts.

Some experiments which I made in co-operation with Estermann¹ on the formation of small mercury crystals from pure vapour at low pressure gave us the first hint. On the basis of the well-known formula for the velocity of condensation of pure vapour it was to be expected that the velocity of the growth of a small crystal could in no direction exceed a definite maximum which is reached when every incident molecule is condensed. Our experiments showed the surprising result that the velocity of the growth in certain directions was 1000 times as great as it should have been. The mercury crystals settled as extremely thin hexagonal leaflets which adhered to the wall only at a small spot (prism surface) while their main growth had been into the free space. The prism surfaces showed a velocity of growth 1000 times as great as that which the impact-formula would have led one to expect, while the velocity of the growth of the full-sized basal face remained markedly less than the theoretical maximum. For this surprising fact we offered an explanation which implied several kinetic conceptions then unusual. The first of these suggested that when a molecule strikes a crystal it does not always give off the entire heat of condensation—in contrast with the case of liquids; if it strikes a basal face of the crystal the molecule is bound with less energy than that equivalent to the molecular heat of evaporation. This, at that time, surprising presumption has since been confirmed by calculations made by Kossel² and Stranski³ on the ionic lattice. The second implication was that those molecules which are not yet finally condensed but only adsorbed, can migrate on the surface by virtue of thermal motion, but that they cannot at once leave the surface again because they are bound by the energy given off in the form of heat of adsorption. The mobility lasts until they have reached a place where they are bound with the full heat of condensation. It seems that such a migration, as is assumed here in the case of mercury atoms, is not in evidence in the case of ions on heteropolar crystals.

The interpretation of these experiments cannot be considered as conclusively proved. For there is one (and only one) other possibility, namely that the mercury atoms penetrate into the basal plane and then, as it were, drive the crystal apart from within. We refused to adopt this conclusion, and subsequent experiments have proved that we were right.

An argument in favour of the surface migration theory of the mercury atoms was to be found in the analogy existing to well-known observations on the growth of crystals from super-cooled melts beyond the range of the liquid phase. Such a thing, of course, is possible only if a capillary film of the super-cooled melt can spread across the crystal surface. If the temperature is near the melting-point there is a real fluid film still covering the growing crystal. As the super-cooling progresses the film gradually becomes thinner and at last changes from a condensed mono-

¹ *Z. Physik*, **7**, 13, 1921.

² *Nachr. Ges. Wiss. Göttingen. Mathem. phys. Kl.*, 135, 1927.

³ *Z. physik. Chem.*, **136**, 259, 1928.

molecular to a gaseous film. If one thus has become accustomed to the knowledge that an adsorption film is instrumental in building up a crystal, then it is not a far cry to the idea that a film of correspondingly fewer molecules has its share in the disintegration of a crystal lattice. This presumption could actually be confirmed by experiments of Adhikari ⁴ with benzophenone crystals. Moll ⁵ succeeded in 1928 in performing similar experiments with crystals of phthalic anhydride.

As the solid phase, in contact both with supersaturated and unsaturated vapour, is surrounded by a mobile adsorption film, we have to assume the existence of such a film at the state of equilibrium also. These adsorption films on the crystal faces appear only during the growth or decay of the crystal, and are therefore of less interest than films of adsorbed foreign molecules.

In this way we were led to search for such a two-dimensional mobility also in the case of these foreign molecules. To this end the following experiments were made a few years later in co-operation with Adhikari. ⁶ A glass plate was covered with benzophenone. Along the edge a border of free glass of a few hundredths of a millimetre wide was then made by dissolving the benzophenone with mercury. The edge of the glass was then rinsed with pure mercury that was constantly dropping off. Although the mercury never came in touch with the benzophenone, nevertheless the weight of the benzophenone decreased rapidly. The process is analogous to the diffusion of dissolved molecules under the influence of a concentration gradient. At the contact of the glass and the mercury, the density of the adsorbed film is nearly zero, while at the edge of the benzophenone it attains the equilibrium value of saturated vapour. This surface density was measured by a special adsorption experiment in the following way: the quantity of benzophenone adsorbed from saturated vapour by a glass plate of a large known surface was driven off by subsequently heating the glass plate, then distilled into a cooled capillary tube and weighed.

In 1928 the experiment was repeated by F. Moll ⁵ in a slightly different way. A very thin film of the substance to be examined was obtained on an object glass. The edge of the glass was again rinsed with mercury dropping off. The diminution of the film could be observed by the change of the interference colours between crossed nicols. Moll tried this experiment with benzophenone and salol, and in both cases was able to show the expected effect.

Estermann ⁷ in 1923 condensed silver vapour on a polished quartz plate. The average thickness of the deposits was less than that corresponding to a monomolecular layer. Ultramicroscopic examination showed that the film was not homogeneous but consisted of scattered crystals; they were easily discernible in the ultramicroscope and so consisted of at least 1000 atoms each. This can only be explained by the fact that the silver atoms equally distributed upon the quartz surface migrated along it.

Within the last few years W. Richter ⁸ and myself have carried out some experiments on the migration over the surface of crystals of mica and diamond, likewise with a positive success. In the case of mica we even determined approximately the influence of the temperature on the migration velocity.

⁴ *Z. Physik*, **35**, 170, 1925.

⁵ *Z. physik. Chem.*, **136**, 183, 1928.

⁶ *Ibid.*, **119**, 46, 1926.

⁷ *Ibid.*, **106**, 403, 1923.

⁸ *Diss. T. H.*, Berlin, 1931.

The following data of a serie of experiments indicate in 10^{-8} grms. the quantity per hour of benzophenone migrating over an area of mica 1 cm. long and 1 cm. wide :

30° C. .	3.58	3.02	4.05	2.87	3.66	6.77	1.97	4.70	2.50	3.60
20° C. .	2.55	1.78	1.77	1.88	2.56	1.68	2.13			

Although the data do not agree well the positive influence of temperature can be easily seen.

We still have to consider that the density gradient was different in the two cases. In order to ascertain this, we determined the amount of benzophenone adsorbed by mica from nearly saturated benzophenone vapour at 30° and 20° respectively. As condensation could take place if the vapour is completely saturated, the vessel containing the mica foil was kept 1° warmer than the vessel containing the benzophenone. The mean values of surface density were :

$$\begin{aligned} \text{at } 30^{\circ} \text{ C. : } & 1.7 \times 10^{-8} \text{ g. per cm.}^2; \\ \text{at } 20^{\circ} \text{ C. : } & 4.9 \times 10^{-8} \text{ g. per cm.}^2. \end{aligned}$$

The adsorbed amount rises by lowering the temperature, which indicates that the heat of adsorption is larger than the heat of evaporation of solid benzophenone. The fall of the density was at 20° about 3.4 times that at 30°.

If we assume the velocity of diffusion to be proportional to the fall of concentration (which, considering the high densities could only be an approximation) we arrive at a six-fold mobility per ten degrees. Even allowing for the uncertainty of the value we can state qualitatively that the temperature coefficient of the surface migration is very high, and that the process must have a mechanism quite different from the diffusion of dissolved molecules. It must also be clearly distinguished from the spreading of adsorbed substances on the surface of a liquid. In this latter case the tendency of the adsorbed molecules to expand is effectively assisted by the molecules of the solvent which push in from the third dimension, *i.e.*, from the interior of the liquid between the adsorbed molecules and thus accelerate their spreading. This phenomenon is essentially to be characterised as a hydrodynamic current.

The following conception of the mechanism of the spreading over solid surfaces would suggest itself: at low enough temperatures the adsorbed molecules, in accord with the original idea of Langmuir, are mostly bound to the fixed atoms of the underlying material, and like these, only oscillate around their equilibrium positions. When, with rising temperature, the amplitude of the oscillations is increased, it will occur more and more often that an adsorbed molecule, because of an occasional elongation, jumps into the unoccupied field of an adjacent atom. The process, therefore, requires a definite energy of activation and its velocity will increase as the temperature rises in accordance with an exponential law.

This theory is qualitatively in good accord with the observations made by J. Becker⁹ on the thermionic emission by a tungsten ribbon which was covered on one side by adsorbed barium or caesium. Below 900° T. the emission of the uncovered side of the ribbon, as compared with the activated side, was infinitesimal, even after many hours. But

⁹ *J. Amer. Electrochem. Soc.*, **55**, 153, 1929.

above this temperature the emission of the covered side decreases rapidly, while the emission of the uncovered side rises, until finally, after reaching a stationary state they become equal. The phenomenon proves that the adsorbed Ba or Cs atoms spread uniformly on the surface, and that the temperature favours the migration.

Similar experiments have been carried out by Langmuir * with tungsten filaments covered with oxygen. He arrives at the conclusion that a fixed film (two-dimensional solid phase) of oxygen atoms is attached directly to the surface of the tungsten. On this solid film a second film of movable oxygen atoms is adsorbed.

For the occurrences observed by Langmuir,¹⁰ in connection with the activation of tungsten filaments by thorium atoms, Gehrts¹¹ gives a new explanation based on the surface migration theory. Langmuir had assumed a diffusion of the thorium atoms from within the tungsten filament. This theory meets with difficulties, since P. Clausen¹² has proved that a filament consisting of a thoriated core mantled by a single crystal of tungsten cannot be activated in the way indicated by Langmuir. Gehrts therefore believes that in the case of ordinary tungsten filaments the thorium atoms come from the interfaces of the crystallites and then migrate over the surface until a uniform density is reached. He is thus able to give even a quantitative interpretation of the activation.

Probably surface migration will, on occasion, have to be taken into account in dealing with the theory of promotor action in catalytic processes, as it favours a migration of the reaction partners towards the three-phase limit.¹³

The migration on the interfaces of solids, *i.e.*, along the fissures of the single crystals of chemically uniform substances or between the contacts of two solid phases, probably plays a part which is more important in natural phenomena and in engineering. This migration is the primary step which has to precede the settling of any substances, *e.g.*, reaction products, in the interior of solid bodies. The very considerable mechanical effects which are occasionally to be noted here are due to the thinness of the interfacial films. An approximate computation will show that a gradient of interfacial tension of only 1 dyne per cm. enables the monomolecular film to penetrate against a pressure of about 30 atmospheres.

Berlin.

* *A Lecture in the Harnack House, Berlin, 1929.*

¹⁰ *J. Am. Chem. Soc.*, **38**, 2280, 1916.

¹¹ *Z. techn. Physik*, **12**, 66, 1931.

¹² *Physica*, **7**, 193, 1927.

¹³ *Naturwiss.*, **14**, 103, 1926.

DEVIATIONS FROM THE "IDEAL" TRANSLATIONAL MOTION OF ADSORBED MOLECULES.

BY M. G. EVANS.

Received 19th December, 1931.

There is abundant evidence of the mobility of molecules in the adsorbed state on solid surfaces.

Bangham¹ from a study of the expansion of charcoal during adsorption has developed an equation relating the pressure of the gas p and the amount of adsorption s :

$$\log p = i \log \frac{s}{\sigma - s} + i \frac{s}{\sigma - s} + \text{constant},$$

where σ is the limiting value of sorption.

This equation is developed on the assumption that the adsorbed molecules are behaving as a two-dimensional gas film obeying the equation $\pi \left(\frac{1}{s} - \frac{1}{\sigma} \right) = iRT$, where π is the two-dimensional pressure exerted by the film.

There is, on the other hand, evidence that, under certain conditions of temperature and pressure, the adsorbed molecules may be more firmly held by the surface; a change which will probably involve the distortion of the adsorbed molecules.

Lennard Jones² has shown that the forces outside a crystal surface may be considered as (a) a long distance force; the Van der Waals' attraction, superimposed on this; (b) more intense forces which fall off rapidly as we recede from the surface, which are electrostatic or polar in nature. Let us imagine that in the case of an ideal surface* the adsorbed molecules are held by means of the Van der Waals' attractive force. If also we assume that the adsorbed molecules are large compared with the fine structure of the surface; that is with the irregularities in the surface attendant on the necessary discontinuity of any solid surface; we can imagine that the adsorbed molecules will move about in a equipotential field near the surface of the solid as a two-dimensional gas film. This is considered to be the state of affairs when the ideal isotherm,

$$\log p = i \log \frac{s}{\sigma - s} + i \frac{s}{\sigma - s} + \text{constant},$$

is obeyed. If, however, there are irregularities in the surface of the solid then the movements of the molecules in the two-dimensional gas film will be fundamentally affected and it is proposed to consider two possible sources of deviation from this ideal state.

¹ Bangham, *J.C.S.*, 1324, 1931.

² J. E. Lennard Jones, *Trans. Faraday Soc.*, 24, 92, 1928.

* By an ideal charcoal surface we mean a surface which does not possess surface irregularities in the nature of imperfectly crystalline patches of activity.

(a) "The Edge Effect."

It is well known that the edges and corners of a crystal show exceptional activity, and also that patches possessing high activity may exist on the true crystal surface due to (a) the mosaic-like nature of a solid;³ (b) the presence of imperfectly crystalline or agglomerate material.⁴

There is abundant evidence that in the early stages of the sorption process these highly active centres are quickly saturated. Molecules of gas adsorbed at such points on the surface will be unable to partake in the movements of molecules in the two-dimensional gas film and we can consider such molecules to be "statically adsorbed."

After the active patches of the surface have been saturated (a process which will reach completion in the very early stages), we can assume that no further part will be played by them in any subsequent process, so that such adsorption will only affect the initial portion of the isotherm, and will not account for any radical changes over the whole process.

(b) The Effect of Points of Secondary Activity on the Ideal Isotherm.

There will be, however, active points on the otherwise plane surface which do not possess sufficient energy to hold adsorbed gas molecules statically, but which by virtue of the higher activity they do possess will be able to impede the free movement of adsorbed molecules in the two-dimensional gas film. Germer⁵ has shown by electron diffraction from nickel surfaces that adsorbed gas molecules may be present in two states on the surface, (a) the adsorbed molecules occupying definite orientated positions with respect to the underlying nickel atoms; and (b) the molecules in random distributions over the surface.

In this case, the points of "secondary activity" bear a definite relationship to the spacing of the nickel atoms in the lattice. This need not, however, be the general case, and in other cases agglomerate formations might constitute the active points.

Germer found that the change over from the two-dimensional gas film to the "gas crystal" state could be brought about by a decrease in temperature, it follows therefore that even in the case of the two-dimensional gas film mobile molecules on approaching these points of secondary activity will have their mobility decreased, and may vibrate about such a point until becoming endowed with sufficient kinetic energy (by collision or increase in temperature), they are able to break away and re-evaporate into the two-dimensional gas film.

The effect of such points in the surface will obviously be to reduce the ideal pressure * of the two-dimensional gas.

Mathematical Treatment.

Let us assume that the points of secondary activity such as we have defined in section (b) possess an average energy level such that in passing from the Van der Waals' field into the more intense field superimposed by virtue of such active points, the energy change is given by λ an average value from which any particular change differs only by a small amount $\delta\lambda$.

³ Smekal, *Z. Elektrochem.*, **35**, 582, 1929; Zwicky and Lennard-Jones.

⁴ Taylor, *Proc. Roy. Soc.*, **108A**, 105, 1925, and subsequent publications.

⁵ Germer, *Z. Physik*, **54**, 408, 1929.

* *I.e.*, the pressure exerted by a film adsorbed on a plane equipotential surface free from points of secondary activity.

Let α be the number of such active points on unit surface, and s the sorption value. Then the number of active points covered at this particular sorption value s will be given by

$$\nu = k\alpha s e^{\lambda/RT}.$$

In expressing the value of ν as a direct proportionality to both the number of active points and the number of gas molecules adsorbed, we have assumed that each point in the surface exhibiting activity of this particular nature has an independent "thermodynamic environment," and hence any change occurring at such points would not in any way affect the energy change accompanying the binding of an adsorbed molecule at any other point in the neighbourhood.

We can now estimate the effect of such active points on the "ideal" two-dimensional pressure exerted by the gas film.

Let π_0 represent the "ideal" two-dimensional gas pressure.

π_1 the actual two-dimensional gas pressure.

i_0 the ideal cohesive factor (mutual cohesion between the molecules).

i_1 the cohesive factor corrected for the surface possessing active patches.

The discussion here is limited to the case where $i_0 = 1$ and is constant throughout the sorption range, and to unit surface area of the sorbent.

The law for the "ideal" case of a two-dimensional gas is given by ⁶

$$\pi_0(A - B) = i_0 RT,$$

where A is the area occupied per adsorbed molecule at sorption value S , and B that at the saturation value of sorption σ . If we assume that the area a molecule occupies when situated at a point of secondary activity is that area occupied per molecule at the saturation value of sorption, then we can express the area covered by molecules devoid of translatory motion as

$$= \nu B.$$

Then the area occupied by mobile molecules

$$= 1 - \nu B,$$

since we are considering unit surface area.

The number of completely mobile molecules

$$= s - \nu,$$

assuming that each active point is covered by only one molecule.

Then the area occupied per molecule by mobile molecules

$$= \frac{1 - \nu B}{s - \nu} = A.$$

Hence, in the presence of points of activity the corrected pressure law becomes

$$\pi_1 \left\{ \left(\frac{1 - \nu B}{s - \nu} \right) - B \right\} = i_0 RT.$$

$$\pi_0 \left\{ \frac{1}{s} - B \right\} = i_0 RT.$$

Hence

$$\pi_1 = \pi_0 \left\{ \frac{s - \nu}{s} \right\},$$

⁶ Rideal, *Proc. Roy. Soc.*, 109A, 57, 1925.

and we may write the corrected two-dimensional gas pressure law as :

$$\pi_1(A - B) = \left\{ i_0 \left(1 - \frac{\nu}{s} \right) \right\} RT.$$

Since $\frac{\nu}{s} = k\alpha e^{\lambda/RT}$ and $i_0 = 1$,

$$\pi_1(A - B) = \{ 1 - k\alpha e^{\lambda/RT} \} RT.$$

The Value of n in the Expression $s = kp^{1/n}$.

Bangham has discussed the application of the Gibb's equation to the two-dimensional gas adsorbed at a solid surface,

$$SRT d \log p = + d\gamma = d\pi_0.$$

Here it will be necessary to use a more general equation to take into account the change in the free energy of the surface due to the influence of the active points. This may be expressed

$$SRT d \log p = d\pi_1 + \phi d\nu,$$

$$RT \frac{d \log p}{d \log s} = \frac{d\pi_1}{dS} + \phi k e^{\lambda/RT}.$$

Where ϕ is the change in free energy accompanying the covering of an active point by an adsorbed molecule which by definition will be independent of the amount adsorbed since each point possesses an independent thermodynamic environment.

TABLE I.

Gas or Vapour.	Surface.	T° C.	ϕ .	Gas or Vapour.	Surface.	T° C.	ϕ .
Ethyl ether	Charcoal	-15	3300	CS ₂	Charcoal	-15	1800
"	"	0	3700	"	"	0	1800
"	"	30	4100	"	"	30	1750
Toluene	"	120	5000	Acetic acid	"	120	1800
"	"	205	4800	"	"	205	1600
CO ₂	"	-76.5	2700	NH ₃	—	0	850
CO ₂	"	0	10,000*	NH ₃	—	30	8430
CO ₂	"	30	10,000- 15,000*				

From the expression $\pi_1(A - B) = i_1 RT$, which we can write

$$\pi_1 \left(\frac{1}{s} - \frac{1}{\sigma} \right) = i_1 RT,$$

and

$$\frac{d\pi_1}{ds} = i_1 RT \frac{\sigma^2}{(\sigma - s)^2}.$$

Hence

$$RT \frac{d \log p}{d \log s} = i_1 RT \frac{\sigma^2}{(\sigma - s)^2} + \phi k \alpha e^{\lambda/RT}.$$

But $\frac{d \log p}{d \log s}$ is the value of the exponent n at any particular value of s , i.e.,

$$n_s = (1 - k\alpha e^{\lambda/RT}) \frac{\sigma^2}{(\sigma - s)^2} + \frac{\phi}{RT} k \alpha e^{\lambda/RT}.$$

* Nearly complete mobility.

Plotting n_s against $\frac{\sigma^2}{(\sigma - s)^2}$, this expression gives a straight line of slope $(1 - k\alpha e^{\lambda/RT})$, and of intercept on the axis of

$$\frac{\phi}{RT} k\alpha e^{\lambda/RT}.$$

The results shown in Table I. give the values of ϕ for a number of substances to which this equation has been applied. In all cases the equation holds over a considerable portion of the sorption values, but as would be expected from the approximate nature of the development, falls off as the saturation value is approached. This deviation may be attributed to the mutual cohesion between the adsorbed molecules becoming significant as high surface concentrations are reached.

The author's best thanks are due to Professor H. S. Taylor and Professor D. H. Bangham for their interest and help in this work.

Manchester University.

THEORIES OF ADSORPTION OF GASES. QUANTUM MECHANICS OF THE REVERSIBLE ELECTROLYTIC CELL AND OF ELECTROLYSIS.

BY R. H. FOWLER.

Received 3rd December, 1931.

1.

I wish to report on a subject, apparently not immediately allied to theories of adsorption of gases, which, however, I take to be a subject of such general importance, in which a rigorous though qualitative application of quantum mechanics has made such a successful start, that its rather more remote connection is easily excused. The theory concerns at least the nature of the interaction between a metal surface and a free atom or ion near it and as such its ultimate importance for theories of adsorption proper cannot be questioned. It is in short the quantum mechanical theory of reversible cells and of electrolysis, which has just been given what appears to me to be a first-class send off by the work of Gurney.¹ By this of course I mean only that Gurney's work gives a simple picture of the elementary atomic processes involved in these systems, which grows naturally without *ad hoc* assumptions out of the general principles of quantum mechanics. I shall not attempt to make all the nice points that Gurney suggests, but shall confine myself to his quantum mechanical description of a simple reversible voltaic cell, followed by his discussion of the complicated phenomena of "over-voltage" shown during the electrolysis of a dilute acid.

¹ Gurney, Part I., *Proc. Roy. Soc.*, **134A**, 137, 1931. Part II. *in course of publication*. Many of the ideas will be found also in the much earlier work of Butler (*Trans. Far. Soc.*, **19**, Part III., 1924), who was probably only prevented from developing substantially the same theory by the fact that quantum mechanics did not then exist!

2. Equilibrium at a Metal Liquid Interface.

Consider Sommerfeld's model of a metal, in which the valency electrons are effectively free, being shared round among a set of positive ions fixed at the lattice points which neutralise their charges. When an ion is removed from the neutral metal, work is done to separate the ion from the net attraction of the electrons and the other ions. Thus the curve of potential energy of an ion along a normal to a metal surface, when the metal is uncharged but may be dipping into a conducting solution (electrolyte), will be of the general form of Fig. 1. There will be a number, perhaps a large number, of discrete energy levels in the dip representing possible states of oscillation.

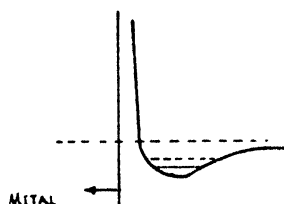


FIG. 1.

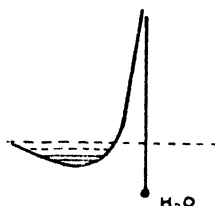


FIG. 2.

There must be a rather similar curve of potential energies for the metal ion near a water molecule [or perhaps, rather, near the complex $(H_2O)_n$] in the neutral electrolyte, since such ions, from their charge and the polarizability of the water molecule, must have a positive heat of hydration. Such a curve is shown in Fig. 2.

When the water molecule is near the surface the two curves overlap and yield a resultant of one or other of the three forms of Fig. 3.

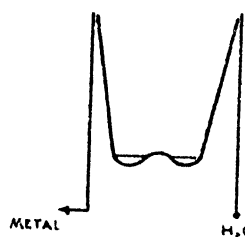


FIG. 3a.

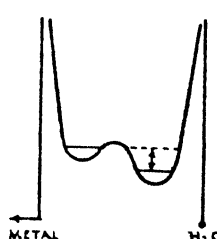


FIG. 3b.

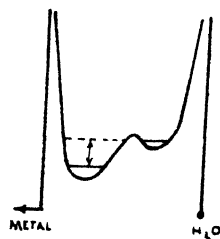


FIG. 3c.

To simplify the exposition we ignore temperature effects, and therefore with the existence of energy levels in the dips other than the lowest (or normal) level allowed by quantum mechanics. The extension can be made without difficulty and involves no new questions of principle. Classically these dips being separated by a barrier of potential energy would represent two distinct positions of equilibrium. But in quantum mechanics no such barrier is complete. The wave function which tries to represent the ion in one dip cannot be confined to the one dip but spreads into the other representing a certain finite chance that the ion will pass through the barrier in unit time into a corresponding level of equal energy on the other side of the bump. In the symmetrical case, shown in Fig. 3a, passages from metal to (H_2O) and (H_2O) to metal are

both possible *and take place reversibly*. In 3(b) passages are only possible from the metal to (H_2O) and in 3(c) only from (H_2O) to metal. In these cases, too, the passage through the barrier first takes place to an excited level on the other side but then de-excitation by collision to the lowest level may take place before return and return is then impossible without reactivation which may be very rare. Thus the passage in these cases is in general *irreversible*.

In the case shown in 3(b) when the neutral metal first dips into the solution ions must leave it and go into solution leaving the metal negatively charged. This negative charge is at once spread smoothly by the free metallic electrons over the surface of the metal, and the excess positive ions in the solution will be held near the surface setting up an electrical double layer (metal $-$, $+$ solution) which raises the potential of the solution and therefore of the (H_2O) levels of the dissolved ions relatively to their levels in the metal. It is clear that this process goes on until we get back exactly to the case of Fig. 3(a), when the processes of solution and deposition can go on at balanced rates.

In the case shown in 3(c) the first action must be a *deposition* of positive metallic ions (assuming them to be available) until a double layer is formed (metal $+$, $-$ solution) sufficient to restore case 3a.

The picture is of course over simplified and probably nothing so precise and clear cut occurs or need occur. The barrier may actually be very small indeed. A more accurate, more blurred picture will give us the same results but will only be harder to comprehend.

Suppose now we have two different metals dipping into the solution which contains the ions of both. Since the solution is a good conductor its potential is everywhere the same and we shall define it to be *zero*. It will differ by a constant (which can be ignored) from the potential of distant free space. If V_1 , V_2 are the potential steps in the electrical double layer that has been set up at either metal surface, negative for 3(b) and positive for 3(c), then *any* standard energy level in the metal 1 for a particle of charge η_1 is higher by $\eta_1 (V_1 + \alpha)$ than some standard energy level in the solution; α is an absolute constant for the solution and the metal depending only on the standards chosen, and not on the state of adjustment, equilibrium or otherwise, at the interface. Similarly the energy levels in metal 2 are higher by $\eta_2 (V_2 + \beta)$. Gurney calls the V 's *interface potentials*. If the standard levels chosen are the normal levels of the metal ion in the metal surface and of the metal ion hydrated in the solution then

$$\alpha = - (V_1)_e, \beta = - (V_2)_e,$$

where $(V_1)_e$, $(V_2)_e$ are the equilibrium values of V_1 and V_2 .

3. Action of the Reversible Voltaic Cell.

When the adjustment described in paragraph 2 has taken place, the whole family of *electron* levels in metal 1 has been raised V_1 in potential above their levels before adjustment, and the whole family in metal 2 raised V_2 . Thus the energies of all the electron levels have been increased by the adjustment by $-\epsilon V_1$ and $-\epsilon V_2$ respectively. The electron levels have been raised $-\epsilon V_1 + C$ and $-\epsilon V_2 + C$ above their levels when the metals are isolated and uncharged in free space, C being the excess of potential in the solution above the potential in free space at infinity. In the normal situation the tops of the Sommerfeld distribu-

tions lie at energy levels $-\chi_1$, $-\chi_2$ respectively, that is χ_1 , χ_2 below the energy of an electron at rest in free space, χ_1 and χ_2 being the thermionic work functions. Thus in the present situation the tops of the electron distributions are, respectively, at energy levels

$$-\chi_1 - \epsilon V_1 + C, \quad -\chi_2 - \epsilon V_2 + C.$$

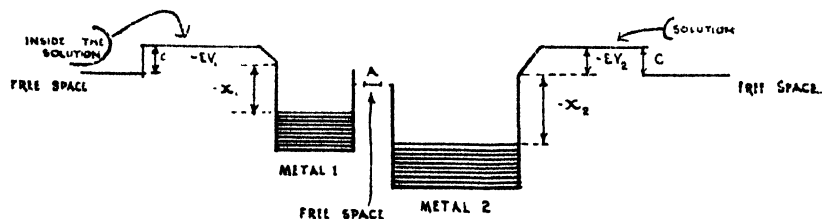


FIG. 4.

Now suppose the metals outside the electrolyte are brought into good contact at A, Fig. 4. Immediately, for the situation of Fig. 4, electrons will flow $1 \rightarrow 2$ and therefore current $2 \rightarrow 1$. This current can only be stopped (short of secondary adjustments such as polarizations or changes of concentration which change the surface conditions in the electrolyte) by inserting such an external e.m.f. into the circuit that we have electron balance at A at the old level difference. This occurs precisely when the tops of the electron distributions are at the same level. We must therefore lift the electron energies in 2 relative to 1 by

$$\chi_2 + \epsilon V_2 - (\chi_1 + \epsilon V_1),$$

electron-volts. The state of affairs at A is then as shown in Fig. 5. This implies raising the potential of 2 relative to 1 by $-E_{12}$ say, where

$$\epsilon E_{12} = (\chi_2 + \epsilon V_2) - (\chi_1 + \epsilon V_1).$$

The potentiometer e.m.f. required for equilibrium is therefore one making 2 positive to 1 by $-E_{12}$. By definition the e.m.f. of the cell is therefore

$$+ E_{12} = \frac{1}{\epsilon} (\chi_2 - \chi_1) + (V_2 - V_1),$$

natural current flowing $2 \rightarrow 1$ outside the electrolyte when $E_{12} > 0$.

It must be observed that

$$C_{12} = \frac{1}{\epsilon} (\chi_2 - \chi_1),$$

where C_{12} is the contact potential difference of the two metals in contact in free space, so reckoned that when $C_{12} > 0$ the potential of 2 is less than that of 1. Thus

$$E_{12} = C_{12} + V_2 - V_1.$$

Moreover though directly observed work functions and contact potential differences are extremely sensitive to surface impurities it is not these sensitive values which are relevant here, but, no matter what the surface contamination, always the values for the pure clean metal. For the

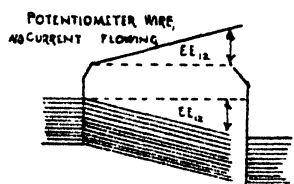


FIG. 5.

vertical displacement of the electron levels in Fig. 4 is determined by the conditions at the metal liquid interfaces from which in a steady state any initial surface impurity will have been removed. Thus even if there are surface layers near A, or for that matter other metal conductors in bulk in the circuit, the same e.m.f. must be inserted there to balance out the flow.

It is in good agreement with the observed facts to say that $V_2 - V_1$ is in general considerably smaller than C_{12} so that roughly $E_{12} \cong C_{12}$ no matter what the solvent of the electrolyte: in particular that the order of the metals in the Volta contact potential series is the same as their electrochemical order determined from the e.m.f.s in electrolytic cells. These facts are of course in happy accord with the foregoing theory. But on the other hand we know from incontrovertible thermodynamic arguments that the energy supply which drives the current, when a current flows, comes from the difference of the heats of solution of the metals. In fact when temperature effects are absent, as in the Daniel cell, we have the almost exact equality,

$$S_{Zn} - S_{Cu} = 2eNE_{CuZn} = 2FE_{CuZn},$$

where F is the Faraday, N the number of atoms in one gram molecule and S_{Zn} , S_{Cu} the heats of solution of one gram molecule of (divalent) ions of Zn and Cu respectively in dilute sulphuric acid. [The exact relationship is of course

$$S_{Zn} - S_{Cu} = 2F\left(E - T\frac{dE}{dT}\right).]$$

It is therefore necessary to ask how this relationship is to be reconciled with the foregoing view which relates E_{CuZn} primarily to the (slightly modified) contact potential difference of the dry contact of Zn and Cu in the metallic circuit.

It is not hard, however, to see that the model proposed does just exactly take care of this relationship. Let us allow the natural current to flow with a good external contact, but only for a short time to avoid secondary polarization effects, and let us consider the ideal limit of negligible electrical resistance in the circuit. Then the electron currents will immediately abolish the difference of energy in the tops of the electron distributions when the metals are joined, and since there is no potential drop in the metals or the solution the whole potential difference E_{12} is transferred to the solution-metal interfaces. The electron potential energies in 2 are raised relative to 1 by eE_{12} and therefore the potential of 2 is lowered relative to 1 by E_{12} . If the potential of 1 is raised relative to the solution by X_1 and that of 2 by X_2 , then

$$E_{12} = X_1 - X_2.$$

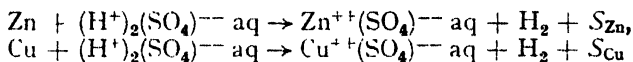
But now suppose for clarity of exposition that the natural current flows in the outside circuit $2 \rightarrow 1$ and therefore in the solution $1 \rightarrow 2$. This current is carried by ions of metal 1, valency z_1 , going into the solution, thereby giving up as heat of solution an energy Nz_1eX_1 per gram molecule dissolved. *The energy given up corresponds to the potential step X_1 no matter what bumps in the potential energy curve may intervene between the ions at home in the metal and the solution.* At the same time ions of metal 2, of valency z_2 , are deposited giving up a heat of deposition $-Nz_2eX_2$ per gram molecule deposited. Solution of z_2 gram molecules

of 1 must accompany deposition of z_1 gram molecules of 2, the total charge moving being $z_1 z_2 F$. Thus the heat evolved is

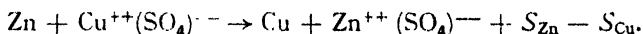
$$N z_1 z_2 e (X_1 - X_2) = z_1 z_2 F E_{12}.$$

The heat evolved in the solution per gram equivalent is therefore just FE_{12} , and the heat evolved in this way must be just the difference of the heats of solution, as required by thermodynamic reasoning, when dE_{12}/dT may be neglected. The essential point is that when the interface potentials have their equilibrium values no heat is evolved on solution or deposition; both processes are reversible and quasistatical. But when the rapid and complete electron adjustment of the potentials has taken place (the resistances being trivial) making changes of X_1 , X_2 in these potentials, then solution and deposition take place irreversibly with an evolution of heat, which is just that corresponding to free falls through these changes of potential. Let us again recall that we have only discussed cases in which there is no temperature effect and no temperature distribution of the ions through a range of levels in the solution or on the metal surface. There is no difficulty in making the extension to the general case where such effects are present.²

In equating FE_{12} to the difference of the heats of solution we have used a special (ideal) method of carrying through the reaction involving the absence of all electrical resistances. But since the heat term involved is an internal energy difference between two definite states it is a matter of no importance by what path the change is made. [For instance for the Daniell cell the heats of solution might be defined calorimetrically by such equations as,



The precise change in which we are interested is



We have carried out this last change in a particular way and must get a heat term $S_{\text{Zn}} - S_{\text{Cu}}$.] From the point of view of the mechanism we have postulated it might be thought that calorimetrically the assumptions of good contact and no resistances are arbitrary and not likely to be fulfilled. But this fear is needless for contact is essential for the replacement of 2 by 1 in the solution to proceed. The electrons left behind in one metal on solution must get round to the other where they are required to neutralise the deposit, otherwise the cell will polarise and the reaction stop. If there are electrical resistances, part of the heat is evolved in the conductors as Joule Heat and exactly that much less at the interfaces. The total evolution of heat, being everywhere of the form (charge passing) \times (total potential drop), remains of the proper invariant form which alone could be acceptable to thermodynamics.

4. Electrolysis. The Behaviour of an Ion near a Metal.

We will now turn to the more ambitious problem of explaining in a similar way according to the principle of quantum mechanics the current voltage relationships (especially for small currents) during electrolysis, including the so-called phenomenon of overvoltage, and in short the detailed experimental laws for the electrolysis of water from a dilute

² Gurney, *loc. cit.*, II., Appendix.

acid on platinum and other *inert* metal electrodes, whose formulation has been completed by the work of Bowden.³

We may start by considering the behaviour of a free atom or free negative or positive ion near a metal surface. If for example the ionisation energy I of the atom or ion is less than χ the work function of the metal, the electron can and will make a transition to an empty level in the metal when the ion is still somewhat off making an actual collision. At fairly close distances such transitions take place quite freely through the potential energy hill. Atoms or negative ions for which $I < \chi$ cannot exist permanently as such near a metal at ordinary temperatures, for there are very few metallic electrons above the level (of depth χ below free space) at which Sommerfeld's set of occupied free electron levels ends, and only such electrons can jump back to the ion. If however $I > \chi$ the positive ion cannot exist as such near the metal, but will be neutralised while still some Angstroms away from the surface. It cannot lose its electron again since the metallic levels at this height are normally full. Thus when $I > \chi$ only neutral or negative ions survive near the metal; when $I < \chi$ only positive ions.

The situation is slightly different for ions in solution since any positive or negative ion in solution has lost energy by interaction with the water molecules compared with its state in free space (*hydration*). This

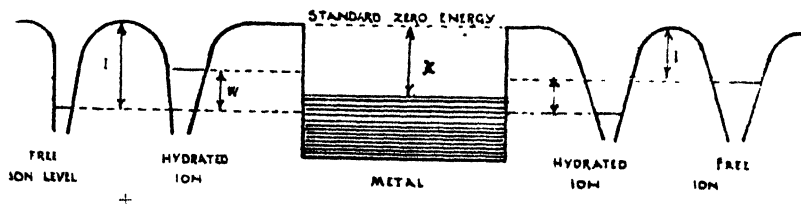


FIG. 6.

loss of energy is of size comparable to the work functions and ionization potentials themselves. This lost energy W must be replaced when the ion is neutralised. The condition for the survival of a positive ion in solution is that there are no suitable metallic electrons of the energy required to neutralise it, that is none of an energy greater by W than those required to neutralise a free ion—that is none of an energy $I - W$ below the standard zero. This condition will be written

$$E_+ = I_+ - W_+ < \chi.$$

The condition for the survival of a negative ion is that the level to which the electron wants to jump shall be full. The electron must take with itself the energy of a level $I + W$ below the standard zero. Hence survival is possible if

$$E_- = I_- + W_- > \chi.$$

The conditions

$$E_+ > \chi, \quad E_- < \chi$$

are the conditions that electron transfers shall be possible to discharge positive and negative ions respectively so that current can flow.

³ Bowden, *Proc. Roy. Soc.*, **125A**, 1929; **126**, 107, 1929. Bowden and Rideal, *Proc. Roy. Soc.*, **120A**, 59, 1928. Bowden and O'Connor, *Proc. Roy. Soc.*, **128A**, 317, 1930.

5. Electrolysis. The Effect of Interface Potentials.

The foregoing paragraph refers to a standard state in which electrical double layers are absent (or have some standard value). When, however, the electrode is an anode so that the positive current must flow from the electrode into the solution and negative ions are being neutralised on the surface, we shall expect to have a double layer set up (metal +, — solution) which will assist the current by assisting the discharge of negative ions by depressing the metallic electron levels relative to those of the solution. The condition for neutralisation is then

$$E_- < \chi + \epsilon V_a.$$

Similarly when the electrode is a cathode and positive ions are being neutralised we shall have a double layer (metal —, + solution) set up assisting neutralisation, so that the condition for neutralisation becomes

$$E_+ > \chi - \epsilon V_c.$$

V_a , V_c are the interface potentials at an anode and cathode respectively.

If either an anode or a cathode is left to adjust itself to equilibrium with the ions in the solution, then it must do so in the way explained in the earlier sections. The ions will be held close to the surface by the image forces and, provided the supply is not limited, will accumulate until they build up such a double layer that neutralization is just possible. The electrode in such a state is *reversible* and for the ideally simple cases discussed so far here the conditions are $E_- = \chi + \epsilon V_a$ or $E_+ = \chi - \epsilon V_c$ respectively. But the reversible electrode can only pass an infinitesimally small current, and in order to pass significant currents we must have the foregoing inequalities. These give the so-called *overvoltages* and the important point to grasp is that these overvoltages are *primary* and essential to the passage of appreciable currents—they are not in any way due to secondary effects such as the need to overcome the resistance of obstructive layers of gas as has often been argued.

A simple general argument shows that electrolysis cannot proceed without building up these interface potentials to some degree; for to proceed with $V_a = V_c = 0$ we must have $E_+ > \chi$ and $E_- < \chi$ (or ideally in the limit $E_+ = \chi = E_-$) and therefore $E_+ > E_-$. But this is impossible in an electrolyte which by hypothesis is a solution in which the state of ionization plus hydration is of lower energy than neutralization, *i.e.*

$$\begin{aligned} I_+ - I_- - W_+ - W_- < 0, \\ E_+ < E_-. \end{aligned}$$

As we have just said when an electrically neutral surface is immersed in the electrolyte both positive and negative ions are attracted to the metal by the image forces so that the surface concentration of ions of both signs is greater than in the body of the solution. But if the metal is made positive with respect to the solution negative ions are more strongly held than positive and their concentration increases at the expense of the positives. This double layer accommodates the applied potential difference V_a between the metal and solution, which is thus confined to a surface double layer (metal +, — solution) which assists in the neutralisation of negative ions. Bowden's measurements show that the total transient current required to build up an overvoltage of say one volt is almost exactly the charge required to establish this potential difference between the plates of a condenser whose area is that of the

electrode, whose separation is about 2×10^{-8} cm. and whose dielectric constant is unity.⁴ The excess number of ions required is of the order of 3×10^{13} per cm.² and the total number in the surface layer may well be 10^{15} , so that the relative change is small. There is little doubt that these extra interface potentials are present, being superposed on those necessary for the reversible state, and are built up by the accumulation of ions until the conditions are adjusted to carry the proper steady current.

6. Electrolysis. Theory of the Current-Voltage Relationship.

We can now see how the theory leads at once to a current-voltage relationship of roughly the right type. We consider throughout only the current to a single electrode whose potential relative to that of the solution is fixed by measurement relative to the potential of an undisturbed electrode carrying no current in another part of the solution. Current can only flow when the electrode is cathode (positive current solution \rightarrow electrode) if

$$E_+ > \chi - eV_c,$$

or when an anode if

$$E_- < \chi + eV_a.$$

If we start applying a voltage making the electrode a cathode say when the electrode is in a state different from that of the reversible cathode, then at first no current will flow in the electrode. As soon, however, as the voltage V_c exceeds $(\chi - E_+)/e$ the current can immediately jump to a large value. But this is just what we require when we remember that our formulation has so far ignored all temperature distributions over a range of energy levels, taking all energy levels or limits of levels as ideally sharp, as they would be at zero temperature.⁵

Actually the hydrated ions instead of lying in a sharp energy level or sharply bounded band, will be distributed over a wide band of energies almost continuously and the distribution must be given approximately by Boltzmann's law. The spread lies in the hydration energy W . Thus if $N_+(E)dE$ is the number of positive ions with neutralisation energy between E and $E + dE$,

$$N_+(E) = N_0^+ e^{(E_0^+ - E)/kT} \quad (E > E_0^+ = I_+ - W_0^+), \\ = 0 \quad (E < E_0^+),$$

where W_0^+ is the (negative) energy of the ground state of the hydrated ions. Similarly

$$N_-(E) = N_0^- e^{(E - E_0^-)/kT} \quad (E < E_0^- = I_- + W_0^-), \\ = 0 \quad (E > E_0^-).$$

Strictly there may be weight factors multiplying the exponential factors by some simple polynomial in E , but these prove to be without much importance at present.

⁴ Though water has a dielectric constant of 80 in bulk, the water dipoles will be fully orientated by the ions, and a dielectric saturation effect will set in, so that the constant will have far less than its bulk value.

⁵ If for a moment we cease to concentrate on a single electrode and consider the cell as a whole this point can be made yet clearer. The voltage applied to the cell is $V_c + V_a$. Current can only flow if $eV_c > \chi - E_+$, $eV_a > -\chi + E_-$, that is if $eV > E_- - E_+$. Once this condition is satisfied we get a sudden increase of current.

In the same way the metallic electron levels are not all full below χ , or all vacant above. The Sommerfeld distribution law, accurately enough for present purposes, gives for the number of electrons $n(w) dw$ of kinetic energy between w and $w + dw$,

$$\begin{aligned} n(w) &= Aw^{\frac{1}{2}} e^{(w^* - w)/kT} & (w \geq w^*), \\ &= Aw^{\frac{1}{2}} \{1 - e^{(w - w^*)/kT}\} & (w < w^*). \end{aligned}$$

The region $w \cong w^*$ in which these formulæ do not hold is not important here. The level of kinetic energy w^* corresponds to a total negative energy χ when there is no interface potential, or $\chi - \epsilon V_c$, $\chi + \epsilon V_a$ when there is one. More explicitly we can write for the distribution law for electrons of given total (negative) energy E , neglecting the unimportant weight factor $w^{\frac{1}{2}}$,

$$\begin{aligned} n(E, \chi - \epsilon V_c) &= A e^{(E - \chi + \epsilon V_c)/kT} & (E < \chi - \epsilon V_c), \\ &= A \{1 - e^{-(E - \chi + \epsilon V_c)/kT}\} & (E > \chi - \epsilon V_c). \end{aligned}$$

Similarly the distribution law of empty electron levels in the anode can be written

$$\begin{aligned} \nu(E, \chi + \epsilon V_a) &= A' \{1 - e^{(E - \chi - \epsilon V_a)/kT}\} & (E < \chi + \epsilon V_a), \\ &= A' e^{-(E - \chi - \epsilon V_a)/kT} & (E > \chi + \epsilon V_a). \end{aligned}$$

In order that appreciable current shall flow at a cathode it is necessary that $N_+(E)$ and $n(E, \chi - \epsilon V_c)$ should have an appreciable overlap. At ordinary temperatures $N_+(E)$ and $n(E, \chi - \epsilon V_c)$ fall to very small values within a tenth of a volt of E_0^+ and $\chi - \epsilon V_c$ respectively, but while N_+ diminishes exponentially as E increases, n increases by the same factor until E reaches $\chi - \epsilon V_c$ when further increase stops. Thus if $P(E)$ is the probability of a jump per unit time by an electron of energy E from the metal to a positive ion (strictly speaking $P(E)$ must be averaged for all distances), we can express the current i which flows at a cathode in the form,

$$i_c = \int_{E_0^+}^{\chi - \epsilon V_c} n(E, \chi - \epsilon V_c) N_+(E) P(E) dE.$$

The conditions for an anode are similar. We require an appreciable overlap of $\nu(E, \chi + \epsilon V_a)$ and $N_-(E)$, and the current at an anode can be expressed in the form,

$$i_a = \int_{\chi + \epsilon V_a}^{E_0^-} \nu(E, \chi + \epsilon V_a) N_-(E) P'(E) dE.$$

These integrals are easy to evaluate approximately and give

$$\log i_c \cong \frac{E_0^+ - \chi + \epsilon V_c}{kT}, \quad \log i_a \cong \frac{\chi - E_0^- + \epsilon V_a}{kT}. \quad (A)$$

It is an experimental fact that

$$\frac{d \log i}{dV} = \frac{\alpha}{T},$$

where α is a constant independent of the nature of the electrodes and of whether the electrode is used as anode or cathode. Numerically α is very close to $\epsilon/2k$ —that is about half the value given by this version of the theory.

Again it is an experimental fact that

$$\frac{d \log i}{dT} \cong 0.05 - 0.06 \quad (T, 287 - 353^\circ K),$$

and that this value decreases with increase of V . The theory gives this change with V and a numerical value of about 0.11 if the numerator is about 1 electron-volt—a range of the proper order of magnitude.

The theory thus is so far almost but not quite completely successful. Complete numerical success is attained if we recognise one theoretical point hitherto overlooked, namely the Franck-Condon principle. In order to neutralise a positive or negative hydrated ion by supplying an electron we may not be and in general are not able to dissociate it into a water molecule and neutral atom at relative rest, but only into a water molecule and neutral atom with a definite amount of surplus energy, determined roughly at least by the principle that the transition takes place between states of equal separation of the atomic nuclei. The negative energies W of the hydrated ion govern the Boltzmann distribution laws $N_+(E)$ and $N_-(E)$ as before, but the energies that have to be supplied or removed by the electron are greater than these E 's. Over the important range of energies we may suppose that the distribution law energies are a fraction $1/\gamma$ of the energies to be supplied, where it is necessary that $\gamma > 1$.

It is not necessary to go into details. The result is easily shown to be to add a factor γ to the denominators of equations A , and there is no reason to believe that the value of γ may not be 2 which will at once give complete agreement between the theory and Bowden's results.

7. Conclusion.

It must I think be agreed that the applications of the general principles of quantum mechanics without any need for elaborate calculation are extremely satisfactory in more ways than one. It is of course most agreeable to have a sound theory of these phenomena of electrolysis and the reversible cell. But it is also most satisfactory to find that quantum mechanics can be used in this quite general way to throw light into a region of physics and chemistry where the mechanisms involved have hitherto been somewhat obscure.

To return finally to the neglected theory of adsorption. The lesson that I think should be drawn from the theory we have just discussed is the importance of interface potentials, the tunnel effect and the Franck-Condon principle. [The tunnel effect is the rather pleasing name given to the penetration through a region of negative kinetic energy.] We learn also that it is probably possible, given sufficient insight into general principles, to go a long way in unravelling surface phenomena without elaborate calculation.

THE MECHANISM OF OVERVOLTAGE AND ITS RELATION TO THE COMBINATION OF HYDROGEN ATOMS AT METAL ELECTRODES.

By J. A. V. BUTLER, D.Sc.

Received 31st December, 1931.

In a recent paper on the Quantum Mechanics of Electrolysis,¹ Dr. R. W. Gurney has calculated the rate of transfer of electrons between an electrode and dischargeable ions in a solution, and has developed on this basis a general theory of overvoltage. His calculation is based on the postulate that "the effect of an electrode potential V is to reduce the work function at the cathode effectively to $\phi - V$, or to increase that at the anode effectively to $\phi + V$." I made use of this concept in 1923 in a "Kinetic Theory of Reversible Oxidation Potentials at inert Electrodes"² and, employing classical statistical mechanics, gave the rate of transfer of electrons to reducible ions present in the vicinity of the electrode at a concentration x as

$$\theta_1 = kxe^{-\phi + EF/RT} \quad . \quad . \quad . \quad . \quad (1)$$

(where E has the opposite sign to V). At the reversible electrode potential, I pointed out that electrons must be returned to the electrode from the reduced material at the same rate, and regarding the reversible potential difference as that required to effect the balance of these two processes, and taking account of the possibility of adsorption of the electromotively active substances, I derived by statistical methods the thermodynamic relations between the electrode potential and the concentrations of the substances or ions taking part in the exchanges.

Under conditions in which the rate of the reverse process is relatively slow, (1) might have been expected to give the relation between the current density and the overvoltage, but the difficulty was encountered that the exponential term required by the experimental data was half that which appears in (1). Dr. Gurney has recently applied the principles of Quantum Mechanics to elucidate the rate of transfer of electrons, and taking into account the forces between the discharged hydrogen atoms and the solvent, has deduced the expression

$$i = kTe^{E_0 - E_1 + FV/\gamma RT} \quad . \quad . \quad . \quad . \quad (2)$$

which may be written, since k contains the concentration of hydrogen ions in the solution

$$i = k'[H^+]Te^{E_0 - E_1 + FV/\gamma RT}, \quad . \quad . \quad . \quad . \quad (3)$$

where E_0 and E_1 are constants, and i is the current density for the potential difference V . γ is a constant which is greater than unity; if its value is 2, the experimental findings³ are accounted for.

¹ *Proc. Roy. Soc.*, **134A**, 137, 1931.

² *Trans. Faraday Soc.*, **19**, 734, 1924.

³ *Proc. Roy. Soc.*, **120A**, 59, 1928 (Bowden and Rideal); **126A**, 107, 1929 (Bowden).

In this expression no account is taken of the rate at which electrons are returned to the electrode by hydrogen atoms. By analogy with (3) we may write this in the form

$$i' = k''[H]Te^{E' - FV/\gamma RT}, \quad . \quad . \quad . \quad (4)$$

where $[H]$ is the concentration of hydrogen atoms at the surface of the electrode. When no current is passing $[H]$ will be governed by the concentration of hydrogen molecules in the solution, and will be determined by the dissociation of molecular hydrogen as in the equation $H_2 = 2H$. We can represent this equilibrium provisionally as governed by the equation $[H_2] = k'''[H]^2$. When a current is passing hydrogen atoms will accumulate at the electrode until their rate of recombination to form molecular hydrogen (and loss by diffusion, etc.) is equal to their rate of formation.

The total current of electrons passing from the electrode to the solution is therefore

$$i = k'[H^+]Te^{E_0 - E_1 + FV/\gamma RT} - k''[H]Te^{E' - FV/\gamma RT}, \quad . \quad (5)$$

where $[H]$ is thus determined. Collecting the constants and putting $\gamma = 2$ in each term, we may write this in the form

$$i = K[H^+]e^{FV/2RT} - K'[H]e^{-FV/2RT} \quad . \quad . \quad (6)$$

Therefore, if $V_0 = 0$ when $i = 0$, we have

$$FV_0/RT = \log K'[H]K[H^+], \quad . \quad . \quad . \quad (7)$$

or

$$V_0 = RT/F \log K'\sqrt{[H_2]}K[H^+], \quad . \quad . \quad (8)$$

which is the usual thermodynamic expression.

As V increases the first term in (6) increases rapidly, and the second diminishes, and unless $[H]$ becomes very great the second term cannot be of any importance in the determination of i for comparatively large currents. But it becomes important for very small values of i . When V is not far removed from the equilibrium potential V_0 , we have approximately

$$i = K[H^+]e^{FV_0/2RT} \cdot F(V - V_0)/RT \quad . \quad . \quad (9)$$

i.e., overvoltage varies linearly with the current density for very small values of the latter.

In collaboration with Mr. G. Armstrong, experiments have been made in this laboratory on the overvoltage produced at platinum cathodes by small currents of the order of 10^{-8} to 10^{-7} amps./cm.², and we have found that in this region the overvoltage varies linearly with the current as is required by this expression. We have also found that a similar relation holds for the discharge of other ions, etc., at the cathode, e.g., in the reduction of ferric salts, of methylene blue, and of quinone, in solutions containing also the reduced substance, for small currents the displacement of the potential difference from the reversible value is approximately proportional to the current density. In these cases a much larger current can be passed before the linearity ceases to hold.

Further, T. Erdey-Grúz and M. Volmer in a recent paper ⁴ have studied the overvoltages required for the deposition of the metals Zn, Cd, Ni, Pb, Bi, Cu and Ag, and find in most cases that the displacement

⁴ *Z. physikal. Chem.*, **157**, 165, 1931.

of the potential difference from the reversible value varies linearly with the current for very small values, and with the logarithm of the current at higher values, as is required by (6). This equation may therefore prove to be general for electrolytic processes.

The reverse term may also be of importance in determining the decay of the overvoltage. According to the measurements of Bowden and Rideal,⁵ the quantity of electricity required to increase the hydrogen overvoltage by 1 volt is about 10^{-5} coulombs/cm.² If we represent this quantity by B , $-B dV/dt$ must be equal to the rate at which electrons are lost by the electrode at open circuit. If the latter quantity is represented by (2) we have

$$-B dV/dt = kT e^{E_0 - E_1 + FV/2RT} \quad (10)$$

The constants in this expression can be evaluated given a knowledge of the $V - \log i$ curve, and using these values (10) can be integrated. The following table gives the variation of V (measured against the mercurous sulphate electrode) with time, when its initial value is 1.8 volts, as calculated in this way.

V .	t (secs.).	V .	t (secs.).
1.8	0	1.30	4
1.66	0.004	1.18	40
1.54	0.04	1.06	400
1.42	0.4	0.94	4000

Mr. G. Armstrong and I have made a number of experiments on the rate of decay of the hydrogen overvoltage at mercury in sulphuric acid solutions. In one experiment the value $V = 1.42$ was reached in 4 secs., and the value 1.30 in about 400 secs., a much slower decay than that calculated. Bowden has suggested that the persistence of the hydrogen overvoltage is due to the deposition and solution in the mercury of small quantities of the alkali metals present as impurities. In these experiments we had an auxiliary mercury cathode by which the solution was electrolysed for about 30 hours previous to the measurement of the decay at the other electrode, and during part of this time the solution was vigorously stirred. While we have not definitely excluded the possibility of this behaviour being due to traces of alkali metals, we have thus shown that it remains after a fairly drastic treatment to remove such traces.

A slower rate of decay would be given by using (6). Then we should have

$$-B dV/dt = K[H^+] e^{FV/2RT} - K'[H] e^{-FV/2RT} \quad (11)$$

We have seen that during the passage of a large steady current, the second term on the right of this equation is small in comparison with the first. But if the rate of loss of hydrogen atoms at the electrode surface is comparatively slow, the second term will become of importance when V has reached a lower value (V decreases by about 0.4 volts in less than half a second). Thereafter the decay of the overvoltage will be mainly determined by the rate of loss of hydrogen atoms from the electrode.

⁵ Bowden and Rideal, *loc. cit.*

It seems, probably, that this occurs mainly by their combination to form hydrogen molecules. A study of the decay of the hydrogen overvoltage, when effects due to impurities are definitely excluded, would thus throw light on the formation of hydrogen molecules from atoms at the electrode surface. We are at present engaged on experiments of this kind.

*King's Buildings,
West Mains Road,
Edinburgh.*

THEORY OF HEAT EVOLVED IN CAPILLARY CONDENSATION.

BY ERICH HÜCKEL (*Stuttgart*).

Received 9th November, 1931.

It is a well-known fact that in certain cases of sorption of vapours by porous bodies the sorption-isotherm for higher pressures becomes convex with respect to the pressure axis. An example of this is given in Fig. 1, which has been taken from measurements of Williams¹ for the sorption of SO_2 by charcoal at -10° .

This behaviour of the isotherms has not been observed in all cases; it seems that it only occurs when the pores of the sorbent are rather large.

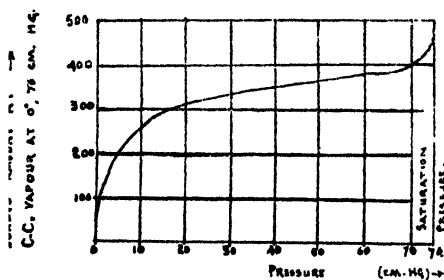


Fig. 1.

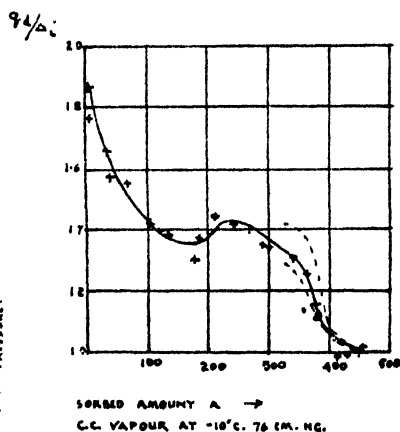


Fig. 2.

The heat evolved in cases where the sorption-isotherm shows the behaviour mentioned has been—as far as we know—determined for pressures near the saturation-pressure only in that one case of Williams. Fig. 2 shows the results obtained by Williams. Here the ratio q_d/Δ_i of the differential heat of sorption (q_d) at -10°C. to the ordinary inner heat of condensation (Δ_i) of SO_2 is plotted against the amount a of sorbed SO_2 .² There is a peculiarity of the curve at about $a = 200$; at this point the curve shows a minimum followed by a maximum, from

¹ A. M. Williams, *Proc. Roy. Soc. Ed.*, **37**, 161, 1916-17.

² The dotted lines are calculated from the isotherm. See later.

which it falls off continuously to the ratio unity. That is to say that the heat of sorption approaches the ordinary heat of condensation.

The heat of sorption can be determined also by taking the sorption-isotherms at different temperatures and applying a relation analogous to the Clausius-Clapeyron formula :

$$q_d = RT^2 \left(\frac{\partial \log p}{\partial T} \right)_a - RT. \quad . \quad . \quad . \quad (1)$$

This has been carried out by Goldmann and Polanyi³ for the sorption of various vapours by charcoal. But there is neither a rise of the sorption-isotherm near the saturation pressure nor the particular behaviour of the heat of sorption, which here falls off continuously over the whole pressure range. But it has to be noted that the charcoal used by Goldmann and Polanyi evidently was quite different from that used by Williams. From the maximum amount of sorbed vapour and the density of the liquid the total hollow space per gr. charcoal can be estimated roughly. It was about 0.98 c.c./gr. charcoal in the experiments of Williams, but only about 0.54 in those of Goldmann and Polanyi. It follows that the charcoal used by Goldmann and Polanyi must have had much finer capillary spaces than that used by Williams. There is thus no possibility of comparing the results of Goldmann and Polanyi with those of Williams.

As to sorption-isotherms of the kind observed by Williams, a theory has been developed by Zsigmondy based mainly on his and his co-workers' experiments on the sorption of different vapours by silica gels: the so-called theory of capillary condensation. The idea of this theory is as follows. For rather small pressures only an ordinary adsorption of the vapour molecules occurs on the surfaces in the capillary spaces of the porous sorbents. With rising pressure these surfaces at first are gradually covered by a thin layer of liquid, and as the pressure continues to rise the capillary spaces are gradually filled with liquid. When the liquid wets the surfaces, the liquid-vapour interfaces in the capillary spaces show a curvature concave to the vapour. Now according to Thomson (Lord Kelvin) the vapour pressure of liquids of concave surfaces is lower than in the case of a plane surface. Therefore the condensation of the vapour in the capillary spaces occurs at pressures below the ordinary saturation pressure. When the capillary spaces are not too small a thermodynamic treatment of this "capillary condensation" is possible.

$$\text{Let} \quad \frac{1}{\bar{r}} = \frac{1}{2} \left(\frac{1}{r_1} + \frac{1}{r_2} \right) \quad . \quad . \quad . \quad . \quad (2)$$

be the mean curvature (Gauss-curvature; $\frac{1}{r_1}, \frac{1}{r_2}$ main curvatures) of

the liquid-vapour interfaces at any point. In the case of equilibrium $1/\bar{r}$ must be the same for all points of all liquid-vapour interfaces, since at a given temperature the vapour pressure depends on $1/\bar{r}$ only. Neglecting certain items the following formula holds:—⁴

$$\bar{r} = \frac{2\sigma v_l}{v_s p_s \ln \frac{p}{p_s}} \cong \frac{2\sigma v_l}{RT \ln \frac{p}{p_s}}; \quad . \quad . \quad . \quad (3)$$

³ F. Goldmann and M. Polanyi, *Z. physikal. Chem.*, **132**, 321, 1928.

⁴ The temperature must be sufficiently below the critical temperature, and $\frac{p_s - p}{p_s}$ not too great.

capillary-constant, v_l, v_v molar volume of the liquid and of the vapour respectively, p equilibrium pressure, p_s saturation pressure, R gas constant, T absolute temperature.)

By identifying \bar{r} with the order of magnitude of capillary spaces filled up at p, T , it is possible to determine this order. Of course, formula (3) can be applied only when values of \bar{r} result which are not too small (e.g., at least more than a few molecular diameters), since it has been derived by the thermodynamical conception of surface tension, which holds only for not too small dimensions of the liquid.

From the sorption-isotherm of Williams⁵ for SO_2 on charcoal at -10° we find the values of \bar{r} given in Table I.

TABLE I.

p (mm. Hg.).	a (c.c. Vapour of SO_2 at 760 mm. Hg per gr. Charcoal.)	$\bar{r} \cdot 10^8$ (cm.)
760 (Sat. Press.).	~ 500	∞
750 "	450	862
700 "	405	145
600 "	380	51.5
500 "	365	29.0
400 "	350	18.9
300 "	310	9.1

Below the sorbed amount of about $a = 350$ the thermodynamical calculation of \bar{r} must be meaningless, since $\bar{r} = 10 \times 10^{-8}$ cm. corresponds to a thickness of about three molecule diameters only. $\bar{r} = 10 \times 10^{-8}$ cm. corresponds here to about 64 per cent. of the sorbed amount at saturation pressure. It may be noted that Goldmann and Polanyi from their measurements obtained $\bar{r} = 10 \cdot 10^{-8}$ cm. for about 80 per cent. of this amount, for which we find \bar{r} more than $100 \cdot 10^{-8}$ cm. This is in agreement with the statement made above that the charcoal used by Goldmann and Polanyi must have had a much finer structure.

The purpose of this contribution is to show that the theory of capillary condensation seems to be capable also of giving an explanation of the heats evolved, provided that the values of \bar{r} are not too small. (This explanation therefore will not be applicable to the experiments of Goldmann and Polanyi.) In particular it will be possible to calculate between certain limits the heat evolved at a certain temperature from the isotherm for this temperature only, whilst generally it is necessary to have at least two isotherms taken for two neighbouring temperatures.

The idea is as follows. The heat of condensation in the capillary spaces will differ from the ordinary heat of condensation for three reasons:—

(1) By the condensation in the capillary spaces the size of the liquid-vapour interface will be diminished. Therefore an amount of surface energy is set free which is proportional to the surface energy $\sigma - T \frac{d\sigma}{dT}$ and the diminution of the surface.

⁵ The surface tension of SO_2 has not been measured at -10° , but at -25° only: $\sigma_{-25^\circ} = 33.3$ dyn./cm. (L. Grunmach, *Ann. Physik.* (4), 4, 367, 1901). By interpolation between -25° and the critical temperature of SO_2 (157°) where σ must be zero one finds $\sigma_{-10^\circ} \cong 30.3$. This value has been used for the calculation of \bar{r} . Further: $v_l = 43.8$ c.c./mol.; $p_s = 760$ mm. Hg at -10° .

(2) The heat evolved per unit of mass of condensed liquid will differ from the ordinary heat of condensation, since according to the curvature of the liquid vapour interface the pressure in the liquid differs from the saturation pressure for a plane surface.

(3) During the condensation the mean curvature of the interfaces changes (diminishes); therefore the pressure in the total liquid already sorbed will change also (it increases). In this manner an amount of compression energy is freed.

There are two difficulties when we seek to calculate the heat of sorption, taking in account these three points. Firstly the angle of contact between the liquid and the charcoal is not known. We shall assume it to be zero, which will be justified by the result. Secondly, it is of importance in connection with point (3) to know whether we have to consider the difference in behaviour between the liquid adsorbed immediately on the charcoal surface and that which is merely condensed, which will have the properties of the liquid in bulk. This difficulty can be overcome by restricting the calculation to two limiting cases. In the first limiting case we assume that the whole amount sorbed behaves with respect to changes of pressure like the liquid in bulk; in the second that the energy content of the adsorbed layer, which may contain the adsorbed amount a_0 , is not changed by changing the pressure in the liquid condensed. It seems evident that the real behaviour of the adsorbed layer will lie between these two limits. According to these assumptions we find for the first limiting case:

$$q_d = \Lambda_i + \frac{2}{\bar{r}} v_l \left(\sigma - T \frac{d\sigma}{dT} \right) - \frac{2T\sigma}{\bar{r}} \left(\frac{\partial v_l}{\partial T} \right)_p + \frac{2T\sigma}{\bar{r}} \left(\frac{\partial v_l}{\partial T} \right)_p \left(\frac{\partial \ln \bar{r}}{\partial a} \right)_T a \quad (4a)$$

and for the second:

$$q_d = \Lambda_i + \frac{2}{\bar{r}} v_l \left(\sigma - T \frac{d\sigma}{dT} \right) - \frac{2T\sigma}{\bar{r}} \left(\frac{\partial v_l}{\partial T} \right)_p + \frac{2T\sigma}{\bar{r}} \left(\frac{\partial v_l}{\partial T} \right)_p \left(\frac{\partial \ln \bar{r}}{\partial a} \right)_T (a - a_0). \quad (4b)$$

The three terms after Λ_i on the right-hand sides of (4a) and (4b) correspond in the order given to the three points stated above.

TABLE II.

a (c.c. Vapour of o° , 760 mm. Hg per gr. Charcoal).	$\bar{r} \cdot 10^8$ (cm.).	q_d/Λ_i (First (Upper) Limit).	q_d/Λ_i (Second (Lower) Limit).
427.5	350.8	1.030	1.019
392.5	87.1	1.116	1.072
372.5	38.8	1.239	1.146
357.5	22.96	1.318	1.182
342.5	15.85	1.408	1.259
322.5	11.38	1.407	1.288

According to these formulæ two limits for q_d and therefore q_d/Λ_i can be calculated from the one isotherm taking $\left(\frac{\partial \ln \bar{r}}{\partial a} \right)_T$ from the isotherm with the help of formula (3). For the second limiting case it is

necessary to know a_0 . It seems very probable that a_0 corresponds to the point where the peculiarity in the $q_d/\Lambda_t - a$ curve occurs. We therefore take $a_0 = 200$. The results⁶ are given in Table II.

These two limits in Fig. 2 have been plotted as dotted lines. The observed curve falls between them, as is to be expected from the theory; of course it would be possible to get a practical coincidence of the observed and the calculated curve by taking a_0 somewhat different from 200 (smaller), but we do not believe that this would be of great value.

It seems that the conception of capillary condensation in that range of sorption where the \bar{r} calculated are not too small is capable of giving the explanation for the heat evolved.

My object in giving this little contribution which is not very new⁷ is to encourage new experiments on this subject. Of course it is to be expected that the results of such experiments will accord with the theory only in cases when the capillary spaces of the sorbent used are sufficiently large enough to allow of thermodynamical treatment.

* σ was assumed to be $\sigma_{-10^\circ} = 30.3$; $\frac{d\sigma}{dT} = -0.2$ (by interpolation; see above); $v_1 = 43.8$ c.c./Mol.; $\left(\frac{\partial v_1}{\partial T}\right)_p = 0.0745$ c.c./Mol. degree; $\Lambda_t = 5960$ cal./Mol.

⁷ See E. Hückel, *Adsorption und Kapillarkondensation*, Leipzig, 1928.

THE ELECTRICAL THEORY OF GASEOUS ADSORPTION.

By A. MAGNUS (*Frankfurt a.M.*).

Received, 9th November, 1931.

Various attempts have been made to explain the regularities observed in the adsorption of gases on solid surfaces. Most theories intentionally avoid giving a physical interpretation of the forces of adsorption and content themselves with general conclusions based on the supposition of forces of attraction of some kind existing between the gas molecules and the adsorbent, or some particular spots on the latter. This method has the advantage of being mathematically relatively simple. Moreover it is less open to criticism than would be definite ideas regarding the precise physical nature of the forces of adsorption. Nevertheless the more specialised method has its adherents, chiefly because concrete ideas regarding the nature of the phenomenon of adsorption enable conclusions to be drawn, which are capable of being put to experimental proof.

All the concrete physical ideas concerning adsorption¹ up to date rest on the electrical explanation of the van der Waals forces of cohesion due to Debye² for which the obvious connection between the critical data of a gas and its adsorbability served as starting-point. Only very recently have attempts been made to treat the matter from the stand-

¹ E. Jaquet, *Fortschr. Chem., Phys. u. physik. Chem.*, **18**, 1, Nr. 7, 1925; R. Lorenz and A. Landé, *Z. anorg. allg. Chem.*, **125**, 47, 1922; A. Magnus, *Z. anorg. allg. Chem.*, **158**, 67, 1926; *Z. physik. Chem.*, **142**, 401, 1929.

² P. Debye, *Physik. Z.*, **21**, 178, 1920.

point of wave mechanics ;³ but such attempts, as far as adsorption is concerned, have not been developed further. We are still probably very far removed from a quantitative formulation of the laws of adsorption based on wave mechanics. Up to the present the history of physics has always shown that existing conceptions are usually not completely superseded owing to advances in theoretical knowledge, but are only extended in the sense that the new theory embraces a larger group of phenomena than the old one. It is only necessary to refer to the development of optics or to the kinetic theory of gases, which, under the simple assumption of a uniform velocity for all gas molecules, leads to practically the same formula as is yielded by Maxwell's more rigid treatment. In this sense the electrical theory of gaseous adsorption is also to be regarded as a valuable working hypothesis, which may possibly be the fore-runner of a more rigid theory. One is led to this view by an unprejudiced consideration of the results which the electrical theory has to show up to the present. These will be discussed in what follows.

The electrical theory of adsorption is based on the fact, that every electrical charge is attracted by an electrically conducting surface. The strength of the attraction can easily be calculated by Kelvin's method of electrical images. It is only necessary to imagine the conducting surface replaced by a mirror image of the charge in the surface, of the same magnitude but opposite in sign. Since each electrically neutral molecule consists of an equal number of opposite elementary charges, each of these must be treated in the manner just described, in order that the attraction of the molecule by the conducting surface may be calculated. The calculation⁴ is particularly simple when the charges in the molecule are not uniformly distributed, *i.e.*, when the molecule is a dipole. If such a dipole may be regarded as rigid, the potential with regard to its mirror image in the surface is calculated to be directly proportional to the square of the dipole moment and inversely proportional to the third power of the distance of the centre of the dipole from the surface. In addition there is an orientation effect, which tends to turn the dipole in a position normal to the attracting surface ; for in the formula for the potential there occurs a factor $1 + \cos^2 \beta$, where β denotes the angle of inclination of the dipole to the normal to the conducting surface.

The treatment of the problem for symmetrically constructed molecules meets with greater difficulties. To be sure we also obtain an attraction in the case of carbon dioxide, say, if this is assumed as a first approximation to be a rigid rod having four positive charges in the middle and two negative charges at each end.⁵ But for a monatomic gas such a point of view is inadequate. In general we shall have to assume that the distribution of the charges in the molecule is not rigid, but that deformations are set up in the adsorption field, altering the charge distribution and converting the molecule into a dipole. Such dipoles are called "induced." The calculation can be carried out for the aforementioned model of the carbon dioxide molecule, which in the adsorption field assumes an angular form, the point of which, formed by the tetravalent carbon atom, is turned towards the conducting

³ For example, F. London, *Z. physik. Chem.*, B. 11, 222, 1931 ; M. Born and V. Weisskopf, *ibid.*, B. 12, 206, 1931.

⁴ The calculations mentioned here and below are for the most part to be found in : A. Magnus, *Z. physik. Chem.*, 142, 401, 1929.

⁵ N. Stark and O. Blüch, *Physik. Z.*, 28, 502, 1927.

surface. The moments of the induced dipoles decrease rapidly with increasing distance from the conducting surface; in the carbon dioxide model they are inversely proportional to the fourth power of the distance. Since the moment appears squared in the formula for the potential, we get a variability of potential inversely proportional to the eleventh power of the distance. Hence we are dealing with an attractive force of extraordinarily short radius of action, so that it is not capable of holding more than a single molecular layer on the surface. Only when the induced moments are large and the concentration in the gas space high will the gas molecules in the first layer, by polarising more gas molecules in the free space, be in a position to adsorb a second layer, and so on. This, however, would then represent a gradual transition to the phenomenon of capillary condensation.

In the case of natural dipoles the adsorptive force possesses a greater radius of action. Consequently the effect of the adsorbent on the dipoles of the gas is greater, so that the formation of multimolecular layers may be expected at comparatively low pressures. Moreover it must be borne in mind that in the case of natural dipoles the assumption of a constant moment is at the most an approximation, which probably holds only for very small molecules such as water. In many other cases the moments will in all probability suffer a not inappreciable increase as a result of the adsorption. Accordingly simple relationships, which can be tested experimentally, are more likely to be found in the case of non-polar molecules at moderate concentrations.

The supposition that the surface of the adsorbent is a conductor is fulfilled in the case of charcoal and metals. More particularly wood charcoal has proved eminently suitable for testing the theory, since it possesses an abnormally large specific surface owing to its great porosity. In addition it suffers to a much less degree from the complications which arise in the case of metals.

The first assertion of the theory, which can easily be tested, consists in the statement that, of molecules of similar chemical constitution, those which are dipoles will, under given experimental conditions, be more strongly adsorbed. A comparison of the dipole SO_2 with the rod-shaped molecule CO_2 shows that the former is much more readily adsorbed. Likewise of the three gases CH_4 , NH_3 , and OH_2 the last two, dipole gases, will be much more readily adsorbed than the symmetrical methane molecules. One is tempted, perhaps, to regard this difference in behaviour as being simply due to the van der Waals forces, which operate between the adsorbed gas molecules and which, particularly in the case of the easily condensible, dipole gases, might easily result in appreciable effects owing to the increased proximity of the gas molecules in the adsorption space. Nevertheless the treatment of the problem which follows, and which leads to the experimentally verifiable opposite result, negatives this conception.

The further development of the theory leads necessarily to the following picture of the processes in the adsorbed layer: As long as the concentration of adsorbed gas is small each molecule will be able to move freely about the surface, as in the free space occupied by a perfect gas, since the potential everywhere on the surface is the same. The mean velocity of this motion will be that of a two-dimensional gas at the experimental temperature. In addition, however, the adsorbed molecules will execute vibratory movements perpendicular to the surface, the kinetic energy of which is likewise given by the kinetic theory

of gases. Molecules with abnormally high velocities normal to the surface will be able to escape from it, while others, arriving from the gas space, will be retained. This simple picture leads to the conclusion that at equilibrium the concentrations in the adsorbed layer and in the gas space must be proportional. This regularity is frequently referred to, by analogy, as Henry's law.

As soon as the concentration in the adsorbed layer has risen, owing to a rise in pressure in the gas space, to such an extent that frequent collisions occur between the molecules, the relationships become more complicated. They can be expressed approximately by means of a two-dimensional gas equation, analogous to the van der Waals equation for gases in three-dimensional space. If we denote the two-dimensional gas pressure of the adsorbed layer by π and the surface occupied by one mole by Ω , the uncorrected equation of state will be

$$\pi \Omega = RT \quad (1)$$

π is proportional to the pressure in the gas space, *i.e.*, $\pi = g \cdot p$.

As two-dimensional corrections two quantities α and β are introduced. These allow for the mutual influence of the molecules and their extension in space, in an analogous manner to a and b in the ordinary van der Waals equation. In contrast to the case of a three-dimensional gas, however, α will represent a repulsion, at any rate so far as non-polar molecules are concerned, if the electrical theory holds good. For the induced dipoles in the adsorbed mono-molecular layer must all be parallel and similarly oriented; hence they repel one another. The corrected equation of state will therefore read:

$$\left(\pi - \frac{\alpha}{\Omega^2}\right)(\Omega - \beta) = RT \quad (2)$$

with positive values of α and β . Replacing π by $g \cdot p$ and Ω by $\frac{O}{A}$ where O is the area of the surface of the adsorbent and A the number of moles sorbed, we may rearrange equation 2 in the form:

$$A = \frac{k_1 k_2 p - k_3 A^2}{1 + k_1 p - \frac{k_3}{k_2} A^2} \quad (3)$$

where $k_1 = \frac{g \cdot \beta}{RT}$, $k_2 = \frac{O}{\beta}$, $k_3 = \frac{ORT}{\alpha}$.

Equation 3 has been written in a form closely resembling the equation of Langmuir. It differs from the latter in the term in A^2 which appears in numerator and denominator. Experiment has shown that equation 3 expresses the adsorption of carbon dioxide,⁴ ethylene and acetylene⁶ on charcoal much better than Langmuir's equation. It is particularly significant that the term α , which denotes a repulsion in equation 2 has always been found to have a positive sign. This result provides the strongest support for the electrical theory of adsorption, since no previous theory led directly to the conclusion that the adsorbed molecules repel one another. It should be mentioned that the equation can be subjected to a quantitative test more conveniently in the form:

$$p = A \left(\frac{p}{A} \right)_0 \left(\frac{1}{1 - \frac{\beta}{O} A} + \frac{\alpha}{ORT} A \right) \quad (4)$$

* In publication.

In this form $\left(\frac{p}{A}\right)_0 = \frac{RT}{g \cdot O}$, represents the constant relationship between external pressure and quantity adsorbed in the Henry range, which is in many cases available for measurement.

The results here described are in many cases in contradiction, even if only apparent, to the phenomena observed in the case of films spread out on water. As is well known,⁷ in these cases π - Ω -curves are obtained which can only be expressed by a van der Waals equation; this postulates an attractive force between the molecules. It may, however, be observed, that the molecules spread as a film on water, e.g., the higher fatty acids are anchored with their dipoles in the water and therefore, owing to the high dielectric constant of water, the mutual influence of the dipoles is very much reduced. On the other hand there doubtless exists a marked van der Waals attraction between the long hydrocarbon chains projecting upwards from the surface of the water, and this alone makes itself felt to all practical purposes under the given conditions. The relationships are accordingly so complicated, that observations of films supported on water cannot be directly adapted to gaseous adsorption on charcoal.

On raising the temperature the concentration in the adsorbed layer will be altered as follows. The amplitude of the vibrations normal to the surface increases; consequently the mean distance of the molecules from the surface increases and the induced dipoles are weakened. This results in a strong diminution in the potential and hence in the quantity adsorbed. A further consequence of this is a diminution of their mutual repulsion, i.e., α falls with rising temperature. In representing different isotherms of the same gas by equation 4 it is actually necessary to use a value of α , which decreases rapidly with rising temperature, whereas β may be taken as constant. The calculation of these values from experimental data is naturally not very exact, since they are only correction terms. Nevertheless the values found appear to be, at least qualitatively, fairly certain.

The experimentally observed dependence of the heat of adsorption upon the quantity of gas adsorbed and upon the temperature also supports these conclusions. It is particularly fortunate that we have two independent methods of determining heats of adsorption, namely, direct measurement in a calorimeter and calculation of Q from the equilibrium pressures (p_1 and p_2) associated with a given adsorption at two neighbouring temperatures (T_1 and T_2). For this purpose it is convenient to employ the simplified integrated equation of Clausius-Clapeyron in the form:

$$Q = R \frac{T_1 \cdot T_2}{T_1 - T_2} \ln \left(\frac{p_1}{p_2} \right) (5)$$

From the electrical theory we may expect the heat of adsorption to behave as follows. In the region where Henry's law is obeyed the heat of adsorption is constant (Q_0) at a given temperature. With increasing adsorption Q diminishes because work must be done against the forces of repulsion, and the increasing occupation of the surface acts in the same sense. On raising the temperature a decrease in the heat of adsorption is to be expected corresponding to the decrease in the potential. The experimental results are in complete qualitative agreement. In

⁷ See Schofield and Rideal, *Proc. Roy. Soc., A*, **109**, 57, 1925; **116**, 127, 1926; N. K. Adam, *The Physics and Chemistry of Surfaces*, Oxford, 1930.

particular no increase in the heat of adsorption above Q_0 , the initial value at the lowest equilibrium pressures, is to be observed at a given temperature either in the case of symmetrical molecules or for dipole gases such as SO_2 . If α were negative, *i.e.*, if a normal van der Waals attraction came into play instead of a repulsion, we should expect at first an increase in Q after the initial value Q_0 . Calculations of the decrease $\Delta Q = Q_0 - Q$, *i.e.*, the two-dimensional Joule-Thomson-effect, which must appear as heat when the adsorbed gas is expanded along the surface to infinite dilution, gives approximately :

$$\Delta Q = \left(\frac{2\alpha}{RT} + \beta \right) \pi - \frac{3}{2} \frac{\alpha\beta}{R^2 T^2} \pi^2 \quad (6)$$

This formula represents, however, only a very rough approximation since in its derivation Ω has to be replaced by $\frac{RT}{\pi}$, which is not permissible in the region of greater adsorptions. Since both corrections act in the same sense, making Ω considerably greater than $\frac{RT}{\pi}$, such a calculation is altogether inexact, whereas in the case of a real three-dimensional gas both corrections a and b affect matters in opposite directions and therefore compensate each other to some extent. Equation 6 therefore represents the experimental results only qualitatively; *i.e.*, it represents a parabola instead of the somewhat differently shaped experimental curve.

Extension of the theory to cover the adsorption of a mixture of two gases offers no difficulties of a fundamental nature. Instead of equation 4 we should expect two equations 7 :

$$\left. \begin{aligned} p_1 &= A_1 \left[\left(\frac{p}{A} \right)_0 \right]_1 \left[\frac{1}{1 - \frac{\beta_1}{O} A_1 - \frac{\beta_2}{O} A_2} + \frac{\alpha_1}{ORT} A_1 + \frac{\alpha_{12}}{ORT} A_2 \right] \\ p_2 &= A_2 \left[\left(\frac{p}{A} \right)_0 \right]_2 \left[\frac{1}{1 - \frac{\beta_2}{O} A_2 - \frac{\beta_1}{O} A_1} + \frac{\alpha_2}{ORT} A_2 + \frac{\alpha_{12}}{ORT} A_1 \right] \end{aligned} \right\} \quad (7)$$

The suffix 1 refers to one gas, 2 to the other; p_1 and p_2 are the partial pressures of the components of the gaseous mixture; α_{12} allows for the mutual influence of the two gases in the adsorbed layer. Since the dipoles of the two kinds of molecules may be antiparallel oriented a negative sign is possible for α_{12} . Equation 7 satisfies the necessary conditions that it resolves into 4 when $A_2 = 0$ and the suffix 1 is removed, and also when the two gases are made identical by putting $p_1 + p_2 = p$, $A_1 + A_2 = A$, $\beta_1 = \beta_2 = \beta$ and $\alpha_1 = \alpha_2 = \alpha_{12} = \alpha$.

An experimental investigation into the relationships obtaining has recently been carried out⁸ by adsorbing a mixture of a dipole gas (dimethylether) and a non-polar gas (acetylene) on wood charcoal. The analysis of the gas mixture was performed interferometrically. The results, which are less accurate than those with pure gases, indicate that equation 7 actually holds.

In the development of the theory the adsorbing surface was assumed to be a perfectly smooth plane. It must immediately strike one as remarkable when wood charcoal, the surface of which is estimated to

⁸ In publication.

be many hundred square metres per gram, satisfies this condition, even though to a limited extent. In the case of an ordinary untreated charcoal this condition is not even approximately satisfied. Careful removal of the mineral matter however yields a charcoal capable of behaving in the desired manner.⁹ Nevertheless the result is difficult to understand, since abnormal adsorption relationships are to be expected at the boundaries of the infinitely small elements of surface. The adsorption potential here will be raised owing to the effect of small holes of molecular dimensions¹⁰ or to the presence of unsaturated carbon atoms on the corners and edges, which exert a sort of residual chemical valency force. The latter is not likely to be the case to the same extent with the practically noncatalytic charcoals. Possibly the explanation of Allmand and Chaplin¹¹ for the disappearance of these abnormalities after cleaning is the right one, namely, that the acid treatment of the charcoal removes the greater part of the mineral contents but at the same time, owing to the greater mobility of the dissolved substances, some of these are carried to the active centres, where they remain fixed under the influence of the high adsorption potential. In this case one should perhaps rather speak of a systematic soiling or of a poisoning of the active centres, than of a cleaning.

The results of adsorption experiments on many metals, which as good conductors would be expected to afford support to the electrical theory, point in the same direction. Whereas in the case of gold we obtain roughly the same shaped isotherms as with "cleaned" charcoal, the curves given by a catalytically active iron are completely deformed.¹² Moreover, in contrast to charcoal, we find that adsorption is specific; *i.e.*, certain otherwise difficultly adsorbable gases such as hydrogen are adsorbed preferentially. The hypothesis of free rest valencies coming into play at the corners and edges, gains probability from this type of "active adsorption" on metals. The quasi-chemical compound thus formed is probably to be regarded as the cause of the catalytic activity of the metals. Allmand and Chaplin's explanation of the effect of acid treatment on charcoal would then find its analogy in the well-known phenomenon of the poisoning of catalysts. Freedom of motion is not to be expected for the molecules adsorbed on active centres, in contrast to the state of affairs assumed to exist in "pure" adsorption. For this case we shall be compelled rather to fall back on the views of Langmuir, which assume that a free exchange of molecules can take place between the active centres and the gas space only, not, however, between the active centres directly. Accordingly the technically important problem of "active adsorption" cannot be approached on the lines of the electrical theory of adsorption. The solution appears to be reserved for wave mechanics to supply, since we are apparently dealing with a transition stage approaching that of a non-polar chemical compound. Side by side with active adsorption, however, pure adsorption appears always to occur and this, as far as may be seen, conforms to the demands of the electrical theory.

In addition to charcoal other adsorbents such as silica gel and oxides such as aluminium oxide are frequently used for technical purposes. They, too, possess a great adsorptive power. With such substances

⁹ A. Magnus and H. Kratz, *Z. anorg. Chem.*, **184**, 241, 1929.

¹⁰ See Magnus, *Z. anorg. Chem.*, **155**, 220, 1926.

¹¹ A. J. Allmand and R. Chaplin, *Proc. Roy. Soc.*, **132**, 460, 1931.

¹² Will be published shortly.

the assumption of an electrically conducting surface, which formed the basis of the theory developed above, is not fulfilled. It is worthy of note that on an exact study, the shape of the isotherms obtained with such substances¹³ shows obvious differences compared with the isotherms on charcoal. If, for example, ethylene is adsorbed on a cleaned charcoal, on silica gel and on aluminium oxide,¹⁴ the O° isotherm for charcoal is already practically parallel to the p -axis of an A - p -diagram at an equilibrium pressure of about one atmosphere, indicating that saturation is near at hand. On the other hand in the case of silica gel and aluminium oxide the isotherm is still rising fairly steeply and almost linearly at the same pressure. We are obviously still very far from the saturation point. Mathematically, too, the difference may be recognised, for it is not possible to calculate α and β according to equation 4. Indeed for β imaginary values are often obtained. In the region of small adsorptions, however, the character of the curves is similar to that of charcoal isotherms. In particular at the lowest equilibrium pressures the curves start with a linear portion; i.e., Henry's law is obeyed. The molecular heats of adsorption are but little different from that found on charcoal in this region.

It has not yet been found possible to give a complete explanation or even mathematical formulation of this behaviour; nevertheless observations of the phenomena resulting from systematic heating are found to throw some light on the question of what takes place during adsorption on such oxidic substances, more particularly on silica gel which is the substance which has been most investigated.

If a silica gel containing large quantities of water is warmed slightly "in vacuo," it loses some of its water. The adsorptive power of the gel rises, since removal of the apparently adsorbed water leaves the surface free for other adsorbents. If the temperature is systematically raised in order to push the removal of water further, a state is reached in which the gel has its maximum adsorptive capacity. Further heating then has the opposite effect and the gel loses its adsorptive power, shrinking irreversibly at the same time. After long continued heating at about 1000°C . the gel becomes practically non-adsorbent. The individual processes cannot be sharply segregated, since a smaller rise in temperature can be compensated for to some extent by a longer heating period and improved vacuum. The change-over point in the effect on the adsorptive power of the gel also seems to depend less on the way the gel has been treated than on the amount of water which is left in it. Such a gel may therefore, as is sometimes done, be characterised by its water content.¹⁵ Nevertheless even this is no reliable criterion since the structure of the gel is doubtless strongly influenced by the mode of preparation. All the same, a gel which has been heated for a considerable period at about 1000°C . may be regarded as completely water free amorphous or microcrystalline SiO_2 .

The change-over point, at which the gel possesses its maximum adsorptive capacity corresponds to a relatively small water content.¹⁶ This water, which can only be removed with difficulty, is probably for

¹³ A. Magnus and A. Mueller, *Z. physik. Chem.*, **148**, 241, 1930.

¹⁴ A. Magnus and H. Windeck, *Z. physik. Chem.*, **153**, 113, 1931.

¹⁵ See F. Krczil, *Untersuchung und Bewertung technischer Adsorptionsstoffe*, Leipzig, 1931, p. 10.

¹⁶ McGavack and Patrick (*J. Amer. Chem. Soc.*, **42**, 946, 1920) find for their gels the maximum between 4.8 and 9.9 per cent. water. E. J. Millar (*Chem. met. Eng.*, **23**, 1155, 1920) gives 5 to 7 per cent.

the most part not adsorbed but is present in chemical combination; *i.e.*, we are dealing not with silicic acid anhydride but with silicic acid itself. This view is supported by the interesting observation that on heating a gel on which ammonia has been adsorbed large quantities of water are liberated even at temperatures lower than the previous out-gassing temperature.¹⁷ Apparently the initially adsorbed ammonia displaces the chemically bound water, replacing hydroxyl by amino groups, so that the water produced and now merely adsorbed can easily escape on heating.

From the above considerations it appears at any rate very probable that a strongly active gel or metallic hydroxide contains practically all its water in the form of hydroxyl groups. Such of these as are in the surface form active centres, owing to their strong dipole character, on which gas molecules can be adsorbed. This holds both for natural dipoles and for non-polar molecules, which are polarised under the influence of the hydroxyl groups.

If such a centre is able to adsorb a single molecule only, the adsorption isotherm must be capable of representation by Langmuir's equation or by equation 4 with $\alpha = 0$. The reason that this is not the case can only be that the adsorption potential is different at different centres. Should we reject this explanation, which appears improbable since Henry's law is found to be obeyed at low pressures, a more likely interpretation, which also takes account of the high specific adsorptive power of the silica gel itself, is as follows: Owing to the presence of the hydroxyl groups a gas molecule impinging on the adsorbing surface will be polarised. The resulting attraction brings the molecule into the immediate neighbourhood of a hydroxyl group without, however, definitely fixing it at one spot. Adsorption is therefore not necessarily complete when a gas molecule attaches itself to each hydroxyl group, since two or more molecules distributed around such an active centre will still be attracted, though the resulting potential will be considerably reduced owing to the mutual screening effect. Comparatively high external pressures will therefore be necessary in order to press further molecules into an already well occupied adsorption layer. This means, however, that an approach to a condition of saturation with increasing pressure will take place very slowly, much more slowly than is the case with charcoal with its constant potential surface. The experimental results are explained qualitatively on this hypothesis, but up to the present there is no possibility of subjecting the matter to a quantitative test.

It is obvious that ionic lattices such as sodium chloride may cause adsorption to take place by inducing electrical moments in gas molecules. In this case one might expect to find relationships between the structure of the gas molecules and the lattice constants of the adsorbent. Starting-points for a generalised treatment are, however, difficult to find.

The interpretation of adsorption on substances which are not electrical conductors but which form atomic lattices, *e.g.*, sulphur or diamond, must be left to wave mechanics.

On the whole the electrical theory of adsorption appears to fit the observed facts qualitatively and, in so far as the data available yield to mathematical treatment, quantitatively too, except for the technically important catalytically active adsorption and the special types mentioned above.

¹⁷ A. Magnus and R. Kieffer, *Z. anorg. Chem.*, **179**, 215, 1929.

THE INTERCHANGE OF ENERGY IN COLLISIONS BETWEEN GAS ATOMS AND SOLID SURFACES.

BY J. K. ROBERTS (*Cavendish Laboratory, Cambridge*).

Received 30th November, 1931.

Let us suppose that we have a metal surface in a gas and that there is a small temperature difference between the two. We want to consider the exchange of energy when gas atoms approach and interact with the metal.

The potential energy V of a gas atom at various distances x from the surface of a solid, which we shall assume to be a clean bare metal surface, may be represented by a curve of the type shown in Fig. 1. The nature of the collision of the gas atoms with the solid is to a large extent determined by the magnitude of the quantity indicated by ϕ in the figure. We shall consider three cases¹ which we shall call case I., case II., and case III.

CASE I.—At temperatures sufficiently low for ϕ to be large compared with the mean thermal energy of the gas molecules, practically every gas atom that hits the metal will be held by the attractive forces and will remain for an almost indefinite time forming part of an adsorbed layer. This layer will be formed very

quickly, and, once it is formed, there will be no direct interaction between gas atoms and the metal, but only between gas atoms and adsorbed atoms.

CASE II.—If ϕ is small compared with the mean thermal energy of the gas molecules, such molecules will in general approach the surface, make a collision with it in which there is an exchange of energy, and then fly away again.

CASE III.—At intermediate temperatures where ϕ is comparable with the mean thermal energy of the gas molecules, there will probably be a very restricted range of temperature in which a large proportion of the gas molecules coming up to the solid will be held by the attractive forces sufficiently long to come into thermal equilibrium with the solid,

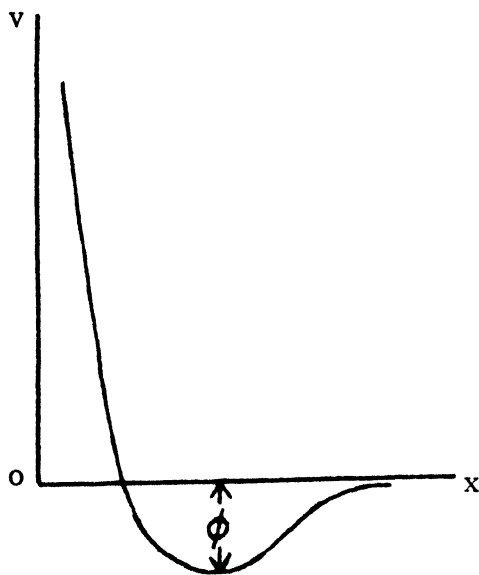


FIG. 1.

¹ See also Johnson, *Proc. Roy. Soc., A*, **132**, 67, 1931.

but not sufficiently long for the probability of a second gas atom's hitting the same part ² of the solid to be appreciable. In this case the exchange of energy will be very nearly complete and the gas atoms leaving the solid will be in thermal equilibrium with it. This is a more definite picture of the process often spoken of as adsorption and re-evaporation.

From the point of view of obtaining knowledge about the mechanics of the interaction between gas molecules and the atoms of a solid we must study case II. To exclude complications due to the rotation of the molecules we shall consider only monatomic gases. If T_2 is the temperature of the metal, and T_1 that of the gas atoms striking it, and if the gas atoms after leaving the metal have on the average energy corresponding to a temperature T_2' , we may write

$$T_2' - T_1 = a(T_2 - T_1),$$

where the constant a is called the accommodation coefficient. If the metal is a wire whose diameter is small compared with the mean free path of the gas atoms, Knudsen ³ has shown that Q the heat carried away from unit area of the wire by the gas atoms in one second is given by

$$Q = 1.74 \times 10^{-4} \frac{pa(T_2 - T_1)}{\sqrt{\mu T_1}} \text{ cal. cm}^{-2} \cdot \text{sec}^{-1},$$

where p = pressure in dynes per square centimetre, μ = molecular weight ($O = 16$). All the quantities in this equation except a can be measured and thus a can be determined.

The surface of the wire must be free from the presence of adsorbed impurities such as oxygen, and this means that the partial pressure of such impurities in the gas must be very low. In working with helium this condition has been fulfilled in experiments that have recently been carried out by continuously circulating the gas through charcoal contained in tubes immersed in liquid air. One such tube was placed at the inlet and another at the outlet of the tube containing the wire. The surface of the wire was cleaned by flashing it to a high temperature. The time zero was taken when this flashing current was switched off and the wire was allowed to cool down to the temperature of the bath in which the containing tube was immersed. When it had attained this temperature a current was passed through it sufficient to raise its temperature ten or twenty degrees above its surroundings and readings of the resistance (from which the temperature could be deduced) and of the time were taken. When the current was first switched on the resistance rose rapidly and then started gradually to fall. From each reading a value of the accommodation coefficient was deduced. The gradual fall in the temperature indicates a gradual increase in the accommodation coefficient due to the gradual adsorption of residual traces of impurity in the gas. By extrapolating the results to zero time the accommodation coefficient for a clean metal surface was obtained. The actual values of the temperature excess of the wire above its surroundings in an experiment with the tube in a bath of liquid nitrogen are plotted in Fig. 2. At the point A the effect of flashing the wire had died out and the temperature of the wire was steady, the small temperature excess being due to the passage of the very small current

² The same part of the solid would be defined as an area equal to the mean area occupied by each atom in the surface.

³ Knudsen, *Ann. Physik*, **34**, 593, 1911.

necessary to measure the resistance of the wire. At this point the current was increased to 5.6×10^{-2} amperes and the temperature rose and then fell. For each point on the part BC of the curve a value of the accommodation coefficient was obtained. At the point C the current was again increased to the value 7×10^{-2} amperes so that the temperature again rose and values of the accommodation coefficient were deduced for each point on the part DE of the curve. These values were all plotted against the time and those obtained from DE lay exactly on a continuation of the curve given by the points on BC.

The results obtained using this technique with helium and tungsten wires differ greatly from those obtained by the ordinary methods which give the accommodation coefficient for surfaces covered with adsorbed films of whose structure and composition nothing is known. In the first place the order of magnitude of the accommodation coefficient is different. The older values for helium at room temperature do not differ appreciably from 0.3, while the value obtained for a clean tungsten

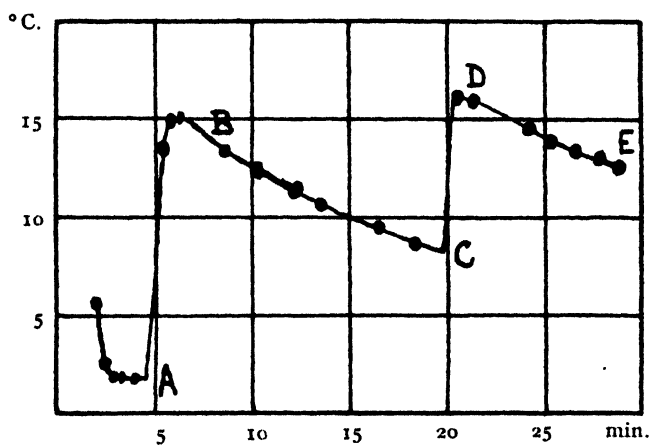


FIG. 2.

surface is 0.057. In the second place the variation with temperature is quite different. The older experiments give a definite increase in the accommodation coefficient with decreasing temperature. For example, for hydrogen and platinum Knudsen⁴ found at 0° C. 0.350, at -79.5° C. 0.376, and at -192° C. 0.423. Similar changes for helium were found by Soddy and Berry⁵ whose values are at about 20° C. 0.28 and in the neighbourhood of -185° C. 0.36. With a clean tungsten surface on the other hand the temperature variation is shown in Fig. 3. It will be seen that at 79° K. the very low value of 0.025 is obtained. The curve suggests that as the absolute zero is approached the accommodation coefficient approaches zero, but at sufficiently low temperatures the thermal energy would become comparable with ϕ for helium and the conditions discussed in case III. above would be realised. At lower temperatures still condensation in bulk would take place, so that the lower parts of the curve would not be realised in practice.

The experiments of Stern and others on the diffraction of atoms by the surface lattice of the atoms of a solid, which have proved that atoms

⁴ Knudsen, *Ann. Physik*, **34**, 632, 1911.

⁵ Soddy and Berry, *Proc. Roy. Soc., A*, **84**, 582, 1911.

of mass m moving with velocity v have de Broglie waves of wave-length $\frac{h}{mv}$ associated with them, show that any detailed theory of the interaction between gas atoms and solids must be treated from the point of view of wave mechanics. The beginnings of such a theory have been worked out by J. M. Jackson in a paper to be published shortly. He has shown that the accommodation coefficient should fall off in value at low temperatures. It is difficult to see how such a result could be obtained from the classical theory.

The following gives a physical picture of the reason for this falling-off at low temperatures. We may regard the solid as an assembly of Planck

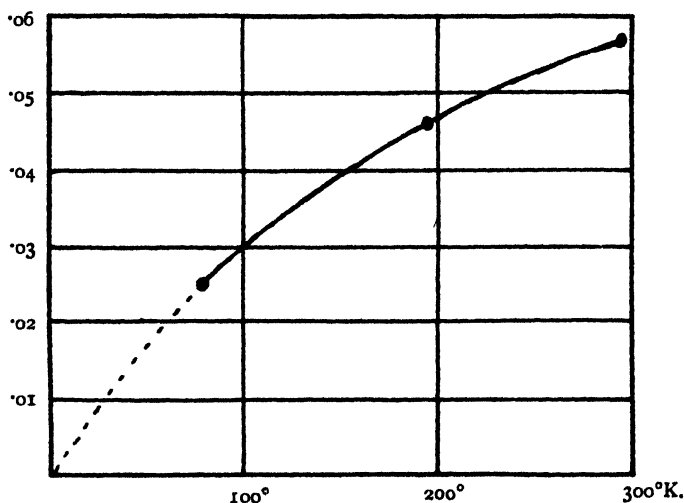


FIG. 3.

oscillators all of identical frequency ν , as Einstein did when he first worked out the theory of the temperature variation of the specific heat of solids. When a gas atom interacts with such an assembly, energy transfers can only take place in amounts of $n h \nu$ where n can have the values 0, 1, 2, 3, etc. At temperatures at which the mean thermal energy is smaller than $h \nu$ a considerable number of the atoms of the solid will be in the ground state. When a gas atom interacts with such an atom the only possible interchange of energy is that the gas atom gives up energy to the solid atom and the smallest amount of energy that it can give up is $h \nu$. The number of gas atoms that have energy $h \nu$ to give up becomes progressively smaller as the temperature gets lower, and thus the proportion of gas atoms which can undergo a change of energy on interacting with the solid becomes smaller and smaller as the temperature approaches the absolute zero.

THE SUGGESTED EXISTENCE OF ACTIVATED ADSORPTION.

BY A. F. H. WARD, M.A., PH.D.

Received 12th November, 1931.

In recent years experimental studies on the sorption¹ of gases on solids have revealed many cases which appear to be exceptions to earlier theories and several different phenomena have been classed together as adsorption. To draw a necessary distinction between cases where different processes are occurring there is some practical advantage in the following classification:

1. The original sorbed gas is recovered completely
 - (a) immediately, on lowering the pressure at the same temperature,
 - (b) only slowly on reducing the pressure at the same temperature, or more quickly on raising the temperature.
2. The original gas is either only partially or not at all recovered on raising the temperature and may appear as a compound of the gas and the adsorbent.

The commonest example of this last case is the adsorption of oxygen on charcoal.

Attention has recently been called to a combination of cases 1a and 1b by Taylor.² It is commonly found in adsorption measurements that at low temperatures (less than 0° C.) sorption occurs instantaneously and that the amount of sorbed gas remains fixed at this equilibrium value as long as the pressure is unaltered. The saturation maximum and the gas sorbed at any given pressure are found to become smaller the higher the temperature. This is the normal process that is universally accepted as true adsorption. If, however, experiments are carried out at higher temperatures, the sorption equilibrium is not reached instantaneously, but a continual fall in pressure occurs in the system,³ and may continue for several months at room temperature.⁴ As the temperature is increased this rate of reaching equilibrium increases and above a temperature of several hundred degrees may become sufficiently rapid for the sorption equilibrium to be attained almost instantaneously on letting in the gas. At a given pressure, the value of this true equilibrium concentration of sorbed gas decreases with rise in temperature, similarly to the decrease observed at temperatures below 0° C., but the values of the equilibrium concentrations at the higher temperatures

¹ In this paper the words "sorption," "adsorption," and "absorption" are employed with the meanings given by McBain (*Phil. Mag.* (6), 18, 916, 1909). Sorption includes all ways in which the gas is taken up by the solid, adsorption refers solely to the gas which is definitely known to be on the surface, and absorption is used in the same sense as solution.

² Taylor, *J.A.C.S.*, 53, 578, 1931.

³ See, for example, Benton and White, *J.A.C.S.*, 52, 2325, 1930, and Gauger and Taylor, *J.A.C.S.*, 45, 920, 1923.

⁴ Ward, *Proc. Roy. Soc.*, 133, A, 506, 1931.

are often greater than those found over the low temperature range. Between these two temperature regions it is impracticable to observe equilibrium values experimentally.

Activated Adsorption or Solution.

It is thus obvious that two different processes are occurring. The process at low temperatures (adsorption) must have a low energy of activation. For the process which needs a higher temperature to make it occur quickly a higher energy of activation must be postulated. What is the nature of this second process? Two explanations have been put forward. Taylor (*loc. cit.*) has suggested that it is "activated adsorption" which is occurring. Experiments made by the author on the sorption of hydrogen on copper have led him to the conclusion that the process occurring at high temperatures with a high energy of activation is solution. It seems desirable to examine critically the evidence which will allow a distinction to be made.

A large amount of evidence has been accumulated that gases are soluble in metals,⁵ and that the rate of solution increases with rise in temperature. It could therefore be confidently expected that whether "activated adsorption" occurred or not, diffusion of the gas into the solid would be a disturbing factor in adsorption measurements, and would give rise to just those irregularities detailed above. At low temperatures where the rate of diffusion was negligible, adsorption (instantaneous) only would be observed, and as the temperature rose, slow solution would be superposed on to the adsorption and cause the equilibrium only to be approached very slowly. At sufficiently high temperatures adsorption would have decreased and the rate of diffusion become sufficiently rapid to make solution the dominant factor. Steacie⁶ has considered the complication caused by solution in adsorption measurements, and has shown that in the majority of cases quoted by Taylor² in support of the "activated adsorption" theory the experimental facts are completely explained by the known solubilities of the gases in the solids considered.

Taylor² gives the following reasons to show that this particular process cannot be solution: "In many of the cases here dealt with the quantities of gas involved are of several orders higher magnitude than the known solubility of the gas in the substance concerned. The surface factor, too, is paramount in the cases we have been considering, whereas this factor is not of such importance where solubility is concerned. The variation of adsorption with pressure is not that to be expected on the basis of solubility." The first of these points has been dealt with by Steacie, who showed "that in almost all the cases cited by Taylor the solubility is quite large enough to account for all the observed facts." He also drew attention to the fact that in a finely divided catalyst a solution equilibrium would be expected to be more rapid than for the material in bulk. This influence of the surface on the rate of solution is considered quantitatively in a later section of the paper, and is shown to be important. The final objection, that the observed variation of the sorption with pressure would not be found

⁵ Sieverts, *Z. physik. Chem.*, **40**, 129, 1907; Sieverts and Krumbhaar, *Ber.*, **43**, 893, 1910; Sieverts, *Z. physik. Chem.*, **77**, 591, 1911; Sieverts and Hagenacker, *Ber.*, **42**, 338, 1909.

⁶ Steacie, *J. physik. Chem.*, **35**, 2112, 1931.

in the case of solubility, is also dealt with below, where it is shown that the solution isotherm has the same form as the adsorption isotherm, *i.e.*, the amount of gas in solution equilibrium is directly proportional to the gas adsorbed on the surface *at the same temperature and pressure*.

Is True Adsorption Activated?

It seems evident from the above considerations that slow attainment of sorption equilibrium at higher temperatures is due to solution, but the question still remains whether true adsorption is an activated process. As Taylor has pointed out, just as we speak of the activation energy of a chemical reaction we may consider adsorption as an activated process. Although for the sake of convenience adsorption is usually referred to as instantaneous, a definite, though small, time must elapse after putting a bare surface in contact with a gas before the adsorption equilibrium is complete. This rate of adsorption, depending on the gas pressure, temperature, accommodation coefficient, mean life on the surface, etc., must have a temperature coefficient from which an activation energy could be calculated. The experimental determination of this would be difficult because of the very small time interval over which pressure changes would have to be measured (probably of the order of 10^{-4} or 10^{-5} sec.), but on account of the great ease of the process the energy of activation of the process would be extremely small.

If, therefore, we accept the idea of an energy of activation for adsorption, it must be applied to true adsorption, and the suggestion that the adsorption process can also take place with a higher energy of activation is as revolutionary as to suggest that the same chemical reaction may in general take place in either of two ways with two different energies of activation. It is not as if adsorption in the form of atoms were possible as an alternative to molecular adsorption. The activation energies of the slow sorption process are not nearly high enough. To take the case of hydrogen, if this were dissociated to atoms on being adsorbed on the surface an activation energy of the order of 90,000 cal. per gm. mol. would be expected instead of such values as 10,000-20,000 cal. per gm. mol. for oxide catalysts⁷ or 14,100 cal. per gm. mol. for copper.⁸

The case of oxygen and charcoal is of particular interest in connection with considerations of activation as this is more nearly allied to chemical reactions than are most adsorption processes. There is a gradual variation from true adsorption at low temperatures to the combustion of carbon in oxygen at high temperatures.⁹ At room temperatures oxygen is adsorbed instantaneously with no lag in reaching equilibrium,¹⁰ but at temperatures of a few hundred degrees the oxygen pressure continues to fall for some time. The speed of this process depends on three factors (at least)—rate of adsorption of oxygen, rate of chemical reaction at the surface and rate of evaporation of the products (CO and CO₂). The activation energy of the process will be largely determined by the slowest of the processes, which the experiments of Rhead and Wheeler⁹ indicate to be the evaporation of the products from the surface. Above

⁷ Taylor and Williamson, *J.A.C.S.*, **53**, 2168, 1931.

⁸ Ward, *Proc. Roy. Soc.*, **133**, A, 522, 1931.

⁹ Dewar, *Proc. Roy. Soc.*, **74**, A, 126, 1904; Rhead and Wheeler, *J.C.S.* **103**, 461, 1913; Blench and Garner, *J.C.S.*, **125**, 1288, 1924.

¹⁰ Ward and Rideal, *J.C.S.*, **129**, 3117, 1927.

about 900° C. this ceases to slow down the reaction, and the CO and CO₂ are apparently removed from the surface immediately they are formed.

Mechanism of the Solution.

Before gas can diffuse into the interior of a metal, it must first be adsorbed on the surface, and until solution equilibrium is reached there will be a resultant flow of gas from the surface inwards. Under the usual conditions of working this will control the rate of solution, as the rate of adsorption from the gas phase is much greater. It has been proved by Wilkins¹¹ for the oxidation of copper that under the conditions when the rate of diffusion of oxygen through the protective cuprous oxide layer was what determined the oxidation rate, this was proportional to the amount of gas on the surface. If, then, this fact is assumed also for the diffusion of gas into a metal, an expression can be derived for the amount of gas in solution at a given time, which can be tested experimentally. Starting from the assumption that the rate of diffusion of gas into the interior of the metal is proportional to the adsorption concentration, the author has derived¹² the following formula for the initial stage of the solution until the centres of the solid particles cease to be free from gas,

$$S = 2ac_0 \sqrt{\frac{D}{\pi}} \sqrt{t}$$

where S is the total amount of gas in solution at a time t , a is the surface area, c_0 is the concentration of gas at the surface, and D is the diffusion coefficient. That is, on plotting the total gas in solution against the square root of the time straight lines should be obtained initially with slopes proportional to the adsorption on the surface (at any one temperature when D is constant).

Experimental Results.

Experiments have been made on the copper-hydrogen system, which is a typical example of the behaviour discussed at the beginning of this paper. The apparatus used has been described in a previous paper,¹³ and the adsorption and solution measured by the change in pressure in a closed system containing the copper and hydrogen. The adsorption isotherm was calculated from the immediate fall in pressure on introducing the gas and the solution from the values of the pressure during its slow subsequent fall. The region of temperature was chosen where both adsorption and solution could be measured. At 25° C. adsorption was followed by solution which continued for several months without attaining equilibrium. The rates of solution increased on raising the temperature, and were measured up to 200° C., but 122° C. was the maximum temperature at which an adsorption isotherm could be determined, as above that temperature the rate of solution was sufficiently great to interfere seriously with adsorption measurements. The solution rate, however, was not sufficient in this range to allow equilibrium to be reached in a convenient time. On this account the proportionality between solution equilibrium and adsorption equilibrium (a necessary consequence of the fact that the rate of diffusion inwards is propor-

¹¹ Wilkins, *Proc. Roy. Soc.*, **128**, A, 407, 1930.

¹² Ward, *Proc. Roy. Soc.*, **133**, A, 522, 1931.

¹³ *Ibid.*, 506, 1931.

tional to the adsorption) could not be tested directly. However, verification of the formula stated above, giving the solution amount at any time, afforded an indirect proof of the truth of this hypothesis.

The results of the various experiments have been plotted—the total solubility (S) against \sqrt{t} , and the slopes of the initial straight portions of the curves (until the gas reached the centres of the copper particles) have been measured. On the theory given above, these values of S/\sqrt{t} should be proportional to the adsorption on the surface. This is shown in Fig. 1, where S/\sqrt{t} (S being expressed in c.c. hydrogen at N.T.P. per 100 gm. copper, and t in minutes) is plotted against the adsorption on the

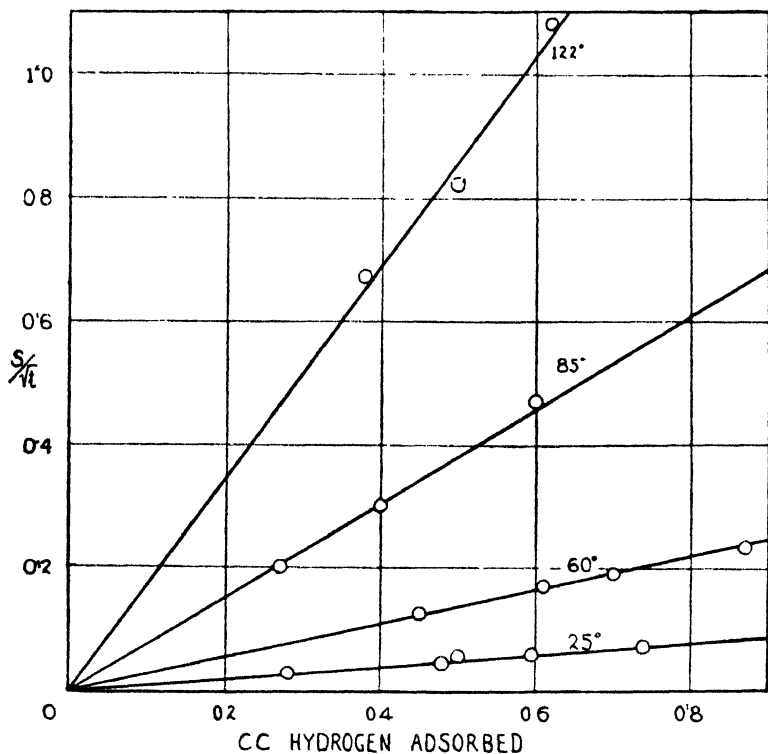


FIG. 1.

surface (c.c. hydrogen at N.T.P. per 100 gm. copper), determined for the various gas pressures of the diffusion experiments from the adsorption isotherm. It is seen that a series of straight lines are obtained, thus confirming the diffusion mechanism developed above. The slopes of these lines, proportional to the square root of the diffusion coefficient, increase with rising temperature, and it is therefore possible to calculate the energy of activation of the diffusion process in the usual way from the variation with temperature of the diffusion coefficient. This value comes to 14,100 cal. per gm. mol.

As was mentioned above, over the temperature range investigated the slowness of the diffusion process made it impracticable to measure the saturation values of the solution. These, however, may be calculated indirectly from solution values before equilibrium was reached.

The general equation for the amount of gas in solution (S) at a time t when diffusing inwards from the surface where there is a constant concentration until the whole volume has the final uniform distribution¹² of gas (amount S_0) is

$$S = S_0 \left(1 - 0.609 \sum_{n=1}^{\infty} \frac{1}{n^2} e^{-kn^2t} \right).$$

This has been applied to the results at 60° C. for gas pressures of 1.9 cm., 6.1 cm., 9.9 cm., and 18.2 cm. A value of $k = 0.0118$ found from some experimental points gives curves which are the same shape as

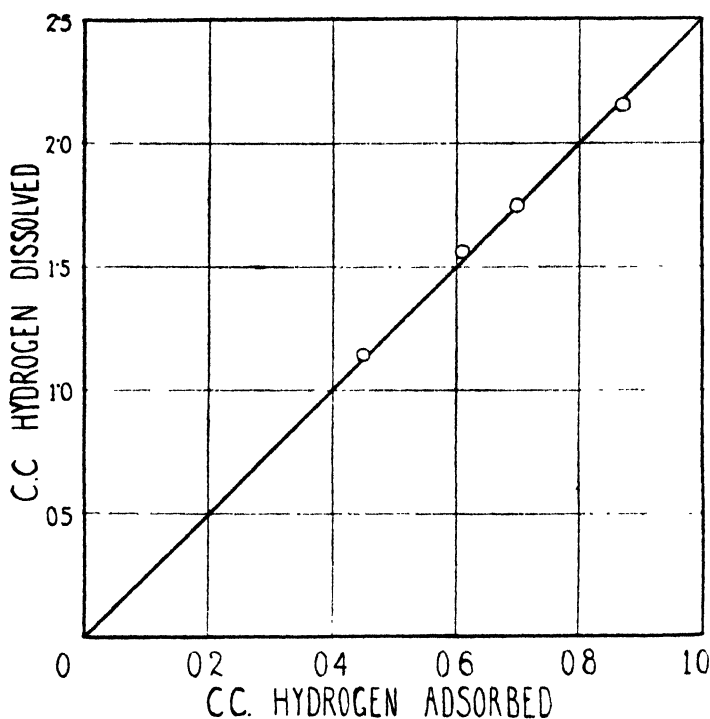


FIG. 2.

those experimentally observed. The values of S_0 determine the scale of the curves and can be found by trial so that the observed points coincide with the curves. According to the theory, these saturation amounts in solution should be proportional to the adsorption on the surface at the corresponding pressures. They are plotted against each other in Fig. 2 and a straight line is obtained.

The Nature of the Solution.

Diffusion of a gas into a solid may occur in two ways, either through the lattice of the solid or along grain boundaries. The first of these will need the atoms of the solid to be sufficiently far apart to allow the gas (atoms or molecules) to pass between. As the temperature is raised and the amplitude of vibration of the atoms of the solid increases a point

will be reached when these are displaced sufficiently from each other so that there is a reasonable probability of the gas passing. This type of diffusion would therefore be expected to become measurable at some critical temperature and to increase in velocity on heating further. As there are greater distances between the solid atoms at Smekal cracks, planes of weakness, etc., the purely spacial factor controlling the diffusion rate will not be so important for grain boundary diffusion. Accordingly it should occur at lower temperatures, and the energy of activation will be that necessary for the lateral diffusion along the surface. Wilkins¹⁴ has interpreted a discontinuity found by Dunn¹⁵ in the activation energy of diffusion of oxygen through cuprous oxide at 650° C. as due to the change from grain boundary to lattice diffusion on raising the temperature. At the temperature of the experiments described here it is most probably grain boundary diffusion which is occurring. As the method of preparation of the adsorbent may cause wide variations in the character of the surface and the internal fissures it is easy to understand the different rates of solution found by different investigators.

Over the temperature range when diffusion occurs along the internal surfaces of fissures in the metal, the total gas sorbed is, strictly speaking, on the surface. But a distinction must be drawn between the two types of surfaces—those which are directly subject to bombardment from the gas phase, and those which can only obtain gas by diffusion inwards along the surface. The line of demarkation must be drawn when the free space between the walls of a fissure becomes of a smaller order than the mean free path of a gas molecule. The term "adsorption" is conventionally limited to the first type—the true externally accessible surface.

Summary.

1. The slow sorption which often takes place at high temperatures has been attributed either to "activated adsorption" or to solution. These alternatives are discussed.
2. It is shown that solution is sufficient to explain the observed facts, and various objections raised by Taylor to the solution theory are shown to be unfounded.
3. True adsorption must have a finite, though small, energy of activation, and it is considered unlikely that the same process could take place in either of two ways with two different energies of activation.
4. Experiments are described on the sorption of hydrogen on copper which give definite evidence that solution occurs. From simultaneous measurements of adsorption and solution at a series of temperatures, it is shown that both the rate of solution and the solution equilibrium are proportional to the amount of gas adsorbed on the surface.
5. A distinction is drawn between adsorption on the externally accessible surface and on the walls of narrow fissures in the solid.

The experimental work described here was carried out in the Laboratory of Physical Chemistry, Cambridge.

¹⁴ Wilkins, *Proc. Roy. Soc.*, 128, A, 407, 1930.

¹⁵ Dunn, *Proc. Roy. Soc.*, 111, A, 203, 1926.

HYDROGENATION OF ADSORBED ETHYLENIC HYDROCARBONS.

BY DR. C. SCHUSTER (*Ludwigshafen a/Rh.*).

Received 26th November, 1931.

Contrasted with many other heterogeneous gas reactions, the kinetics of catalytic hydrogenation has not yet been very thoroughly studied. To be sure, Grassi, and especially Pease and Rideal, have made some very remarkable studies of ethylene hydrogenation. They have observed the total process composed of diffusion, adsorption, desorption, and the actual catalytic processes in the adsorption layer. We have investigated the processes in the adsorption layer itself in order to carry the matter one step forward. In this connection we refer to a recent publication of ours.¹

Active charcoal possesses strong adsorptive powers for ethylene and ethane, more generally for unsaturated and saturated aliphatic hydrocarbons, and a markedly weaker but still measurable adsorptive capacity for hydrogen. Adsorbed olefine is hydrogenated by adsorbed hydrogen in a hydrogen atmosphere. The hydrogenated product remains adsorbed on the surface whilst new hydrogen enters the surface from the gas phase. The decrease of hydrogen pressure in the gas phase is therefore a measure of the hydrogenation of olefine occurring at the surface.

With active charcoal the isotherms for saturated and unsaturated hydrocarbons lie close to one another. With surfaces moderately covered, the adsorption of ethylene and ethane occurs with a heat of adsorption of 7500 cal. per mol. Only when the surfaces are relatively bare are the differences in the adsorption heats of saturated and unsaturated hydrocarbons considerable. Ethylene has then a heat of 16,000 cal., and ethane 10,000 cal. With other substances having extended surfaces, *e.g.*, silica gel, aluminium oxide, Florida earth, the adsorption of the saturated hydrocarbon is markedly inferior to that of the unsaturated.

Hydrogen adsorption at 0° C. on active charcoal follows a linear isotherm over a wide pressure range; with surface relatively bare, the adsorbed amounts increase with increasing temperature with increasing curvature of the isotherms in the first stages of adsorption; with increasing temperature an adsorption process of another kind more and more intrudes as is characteristic for hydrogen adsorption at metal surfaces. For surface areas more completely covered the temperature coefficient of hydrogen adsorption is very small, so that a heat of adsorption of only about 1000 cal. would be involved. Adsorption equilibrium is very rapidly set up; the surfaces of the active charcoals employed in this work amounted to

Medicinal charcoal	8×10^6 cm. ² /g.
Phosphoric acid charcoal	4×10^6 "
Zinc chloride charcoal	7×10^5 "

¹ *Z. physik. Chem.*, 14B, 249, 1931.

In the kinetic experiments these surfaces were only covered to the extent of about 1 per cent.

Ethylene, adsorbed on active charcoal, is hydrogenated in a hydrogen atmosphere in such a manner that, at 0° C., the velocity of reaction, as measured by the fall in hydrogen pressure, is representable as a first order reaction. The velocity of hydrogen consumption is independent of the ethylene concentration in the surface, for each individual experiment as well as for the different degrees of surface covered with ethylene and for the varying initial hydrogen pressures. With constant hydrogen pressure, the reaction is zero order; with very low ethylene surface concentrations the velocity is dependent on the ethylene concentration. Adsorbed ethane does not inhibit the reaction.

The temperature coefficient of the velocity of ethylene hydrogenation in the surface is very small between - 84 and + 50° C. It corresponds to an activation energy of 2000 cal.

Active charcoals of different sorts and different modes of preparation possess hydrogenating capacity for adsorbed olefines. Their capacities, as with other hydrogenating agents, can be measured and characterised by the constants of the velocity of hydrogenation of an adsorbed ethylene layer. The hydrogenation capacity is dependent on the degree of evacuation of the surface. Unactivated charcoals, ordinary wood charcoals, only attain a hydrogenating capacity when upon their surface small amounts of hydrogenating metals are deposited. They share this behaviour with other large surface materials, such as silica gel, Florida earth, etc. On such contact masses the order of reaction is as described above, and the activation energy is of the same order of magnitude.

The study of the hydrogenation of different olefines on the same contact mass (1 per cent. Ni on active charcoal) shows that with increase of hydrocarbon molecule the relations vary somewhat. Propylene behaves like ethylene. The order of reaction is the same, but the hydrogenation is much slower than in the case of ethylene. Thus, for a definite quantity of hydrocarbon, the half-life at 0° C. for ethylene is eight minutes, for propylene it amounts to 104 minutes. The activation energy for propylene is 4800 cal., while for ethylene on the same surface it amounted to 3600 cal. With the three butylenes the course of the reaction is not given by an equation of the first order with respect to hydrogen but, with equimolecular amounts, calculations must be made with the equation

$$dx/dt = k \cdot p^{1.5}.$$

The activation energies are: α -Butylene 6800 cal.; β -Butylene 5600 cal.; *i*-Butylene, 6400 cal., while the half-life periods are: α -Butylene, 228 minutes, β -Butylene, 485 minutes, and *i*-Butylene, 1100 minutes.

For the uncatalysed hydrogenation reaction the activation energy can be estimated from present knowledge to be between 40 and 50 cal. There is therefore a quite extraordinary diminution of activation energy due to the catalyst without the adsorption experiments yielding heats of adsorption of a similar order of magnitude as have hitherto been observed. Here there is, therefore, a case in which the catalytic reaction is practically independent of temperature, without the energy quantities necessary for the reduction of the activation energy being otherwise observed. This suggests the idea that the elementary process in the catalytic hydrogenation of ethylene on the given surface is conditioned by the so-called "Born-Franck mechanism." The average life of the

ethylene molecules on the surface is of the order of minutes. During this time-interval, the molecule is continuously in the neighbourhood of adsorbed hydrogen molecules and the system of the two adsorbed reaction partners degenerates into the desired reaction product. In such cases, quantum mechanics has shown that there is a certain finite probability of escape through the energy barrier without the necessary energy increment. The methods utilised by Born and Weisskopf for the quantitative formulation of this transition probability can be carried over to the present case also and lead, with certain assumptions as to the dimensions of the reacting molecules, to plausible results.

PERSORPTION AND MONOMOLECULAR SIEVES.

BY JAMES W. MCBAIN, F.R.S.

Received 30th November, 1931.

Examination of the mass of experimental data on the sorption of gases by solids¹ indicates that the present term "adsorption" (1881)² has largely outlived its usefulness. As a matter of fact, adsorption upon true unimpaired surfaces has rarely been studied, except upon the meniscus of a liquid. All the solids actually studied have been more or less porous, at least in their outer portions, and most of the actual data refer to solids whose porosity is so extreme as to approach molecular or atomic dimensions. The area of contact between the atoms or molecules of sorbed material in a kilogram of highly activated charcoal, of a dehydrated zeolite, or in Siloxene, and the atoms comprising the structure of the porous solid or crystal, may amount to several million square metres, and the number of sorbed atoms may be almost comparable with the number of atoms comprising the solid structure. The conception of "surface" of such exposed atoms becomes as artificial and forced as the corresponding conception of the "surface" of contact between dissolved molecules and solvent in ordinary liquid solutions. The environment is very similar in the two cases.

Such considerations have led a number of writers to emphasise the likeness of sorption to solid solution. However, this is to lose sight of several real differences between them. In the first place, solution implies that in the course of time every point within the solid will be at some time or other occupied by a molecule of the dissolved substance. This is very definitely not the case with sorption, where the structural material of the solid remains intact and comparatively large spaces are rendered for ever inaccessible to sorbed molecules. In the second place, the diffusive processes which necessarily accompany sorption in the solid mass, occur through ultrapores and along surfaces, and not through homogeneous material postulated in, for example, Fick's law of diffusion in solution. This affects not merely the rates but the amounts of sorption

¹ The author has included an index to about 6000 experimental and theoretical papers in his recent monograph, *The Sorption of Gases and Vapours by Solids*. G. Routledge & Sons Ltd. (London), 3rd December, 1931.

² For reference to the older, now forgotten terms "absorption," "insorption" and "adsorption," see McBain, *loc. cit.*, footnote 4. The term "sorption," now widely used, was introduced by the author in 1909.

which occur in these typically discontinuous solids. Even in the case of rubber, the chains of atomic groupings which constitute the structure remain intact when other molecules are interposed between the chains.

For these reasons, it was suggested by McBain and Britton³ that if a term beyond "sorption" is required, the word "persorption" most clearly emphasises the permeation of the solid by the molecules of sorbed substance without confusing it with true solid solution, such as a mixed crystal or undercooled liquid mixture.

It is evident that this general concept has many implications. One of the most important, now well substantiated, is that sorption is commonly accompanied by expansion or distention of the original solid. This is true of charcoal, even when exposed to unsaturated water vapour, of silica gel, dehydrated zeolite such as chabasite, and metals such as platinum, palladium, iron and tungsten, even when the latter begin as massive metals.

We thus picture charcoal as a conglomerate of cells, micelles and space lattices, a large part of which is permeable by such minute particles as helium atoms. The specific and localised factor which so often accompanies sorption is here represented by the influence of the primary and secondary valencies such as accompany cyclic double bonds. Persorption is essentially monomolecular. Swelling of various materials often goes far beyond any processes of persorption, since it may open up the structure so far as to include tracts of liquid solvent.

Another implication is that of the common occurrence of molecular sieves. The ideal molecular sieve is represented by a crystal of dehydrated chabasite, through which all molecules of less diameter than 3.5 Å. units may freely pass. There is a large number of such porous crystals. Silica gel and charcoal are far less regular than these orderly lattices, but they too function as molecular sieves for sufficiently large molecules or particles such as benzo-purpurine, carmine, etc. Acetate silk behaves similarly. On the other hand, the permeation of palladium by hydrogen may be blocked by water molecules. McBain and Kistler⁴ have published a series of experiments showing how membranes such as cellophane may be made, at will, finer and finer so as to separate, first, molecules from colloidal particles and then smaller molecules from larger ones, down even to the dimensions of water molecules.

As a final illustration of the concepts here described, we may quote the work of Speakman⁵ who has shown that the lamellar micelles in wool fibre are "relatively, if not entirely impervious to molecules as small as the water molecule." Their thickness is of the order of 200 Å., with pores of the order of 40 Å. between them. When the fibre is swollen in water, the length of the fibre is increased 1.1 per cent. and the diameter 18 per cent. Methyl alcohol or methylene glycol enters and swells the fibre, opening the pores until they can admit larger molecules such as octyl alcohol.

Stanford University,
California.

³ J. W. McBain and G. T. Britton, *J. Amer. Chem. Soc.*, **52**, 2198, 1930.

⁴ J. W. McBain, *Colloid Symposium Monograph*, **4**, 7, 1926; J. W. McBain and S. S. Kistler, *J. Gen. Physiol.*, **12**, 187, 1928; *J. phys. Chem.*, **33**, 1806, 1929; *Trans. Far. Soc.*, **26**, 157, 1930; *J. phys. Chem.*, **35**, 130, 1931.

⁵ J. B. Speakman, *Nature*, **126**, 565, 1930; *J. Soc. Chem. Ind.*, **49**, 209T, 1930; *Trans. Far. Soc.*, **26**, 61, 1930.

GENERAL DISCUSSION.

PART I.—EXPERIMENTAL METHODS.

Dr. K. G. Emeléus (*Belfast*) said in reference to Professor Rideal's introductory paper that the possibility of cleaning surfaces by bombardment with positive ions of *controllable speed*, by forming Langmuir positive ion sheaths on them, was perhaps worth further consideration.

Professor E. K. Rideal (*Cambridge*) in reply stated that thermionic bombardment had frequently been employed for cleaning purposes and for fusion.

Dr. R. W. Gurney (*Cambridge*) referring to Dr. Becker's paper said: Quantum mechanics seems to suggest an interpretation of the results in rather different terms from those used by Dr. Becker. When an atom is in free space it must be either exactly neutral, or, if it be an ion, it must bear a charge precisely $\pm n\epsilon$, where ϵ is the electronic charge and n is exactly an integer. But this is no longer true when the atom is within molecular distance of some other atom, for in this case the wave representing the valence electron will not be confined to one atom, but will belong to both. Thus we know, for example, that the HCl molecule has a permanent electric moment, which may be described by saying that one atom bears a charge equal to $+0.16\epsilon$ and the other a charge -0.16ϵ . Fractional charges are also to be expected for atoms adsorbed on to a metal surface, since there is no reason why the square of the amplitude of the wave function, when integrated over the volume of the atom, and summed over all energies, should yield an integral value. If we wish to express this in terms of "orbits," we may say that there are electron orbits lying partly in the adsorbed atoms and partly in the metal, since the potential barrier between them is penetrable to the fast electrons of the metal.

Dr. J. T. Randall (*London*) said: Professor Taylor's remarks in his introductory paper on "The Effect of the C—C Distance on Adsorption of Hydrogen by Charcoals" have interested me considerably. We are at present examining the adsorption of hydrogen on charcoals of different interplanar distances as determined by X-ray measurements. The distance between (002) planes which for graphite is approximately 3.4 Å. can increase to (say, roughly) 4 Å. for a sugar charcoal. According to the theoretical work of Dr. Taylor's colleagues there ought to be an increase in the energy of activation of adsorption as we pass from graphite to sugar charcoal. It will be interesting to see if our experiments confirm this.

Dr. J. A. Becker (*New York*), in reply, said: The results of my paper could quite properly have been expressed by saying that the adsorbed atoms are only partially ionised. It is not clear, though, that quantum mechanics necessarily leads to this picture. The square of the amplitude of the wave function is generally considered to be a measure of the *time average* of charge density at a point. An appropriate integration gives the time average of the moment of an adsorbed particle and in dealing with a large number of particles, it would seem permissible to think of any one particle as being partially ionised all

of the time or completely ionised part of the time. In the latter case, only a certain fraction of the particles are ionised at the same instant. The chief reason for believing that some adsorbed particles are completely ionised is the experimental fact that when caesium is evaporated from a hot tungsten surface sparsely covered with caesium, practically every particle comes off as an ion. Now, if the forces on the caesium adsorbed on the tungsten surface are not sufficient to completely ionise some of the caesium, one would not expect these forces to be sufficient to ionise the caesium when it is farther from the surface and escaping from it. Consequently, no caesium should evaporate as ions unless it was adsorbed on the surface as an ion.

Professor A. Magnus (*Frankfurt*) said: A series of measurements ¹ of mixed adsorption (carbon dioxide and hydrogen at a total pressure of one atmosphere) on a not specially cleaned charcoal showed that the curve representing the amount of hydrogen adsorbed plotted as function of the composition passed through a maximum, corresponding to a hydrogen content of 60 to 90 per cent. With rising temperature the maximum was displaced in the direction of decreasing hydrogen content.

Dr. H. Dohse (*Ludwigshafen*) said in reply: All measurements of mixed adsorption of vapours show that the amounts adsorbed are not additive, but there is no theoretical explanation. Our paper demonstrated a method for such measurements and contains some data, the theoretical explanation of which is not yet possible. A theory of that phenomenon would certainly be of great interest for catalytic scientific work.

Professor W. S. Garner (*Bristol*) said: Mr. Hinshelwood has pointed out the difficulties in arriving at an unequivocal decision as to whether or not reaction chains are started at the walls. Cosslett and the writer ² came to the conclusion that the dried mixture of carbon monoxide on silica gave rise to thermal explosions in which the reaction chains were started at the walls and not in the body of the gas. This was based partly on the fact that the percentage of combustion just above the lower limit depended very markedly on the state of the silica walls. This, as Mr. Hinshelwood points out for the general case, could be explained as due to a variation in the rate of breaking chains on surfaces of different activity. As, however, the preflame reaction was of zero order, it was presumably almost entirely of heterogeneous origin. Thus the mechanism of the ignition of "dried" carbon monoxide mixtures most probably belongs to class I. of the above summary. It was found possible to give a consistent explanation of the action of inert gases on the ignition phenomena on this assumption.

The President said that when installing electrical pyrometers (the first large scale application of which had been made in the ammonium chloride dissociation process worked out by Dr. L. Mond in 1887 to 1889) he had experienced much difficulty in preventing his platinum-rhodium couples from deteriorating on account of the carbon-monoxide which transfused through the iron pipes protecting the pyrometers; he had to substitute pure nickel tubes for their protection. This transfusion of gases through a metal, arising only at increased temperatures, seemed to point to an enlargement of the interatomic spaces which converted adsorption into transfusion, and might throw light on the behaviour of gases at solid surface.

¹ A. Magnus and H. Roth, *Z. anorg. u. allg. Chem.*, **150**, 311, 1926.

² *Trans. Far. Soc.*, **27**, 176, 1931.

Dr. N. K. Adam (*London*), referring to Mr. Hinshelwood's paper, asked : Are any experimental methods available by means of which one can trace, visually or otherwise, the starting and finishing points and the course of reaction chains? If so, we might use them as a new research weapon for investigating the nature and distribution of adsorbed gas layers.

Mr. A. Egerton (*Oxford*) said that in hydrocarbon combustion the view was put forward⁸ that the surface played a double rôle in breaking chains, and also promoting combustion at the surface, the mechanism of the action being similar, but the result different. It was thought that active oxidised molecules might accumulate here and there on the surface, initiating chains, which in turn might be broken at other parts of the surface. There was no doubt that surface adsorption had a close connection with the problem of the initiation of combustion reactions.

Professor E. K. Rideal (*Cambridge*) said that the fact that surfaces may break as well as initiate chains did not appear to suffice to account for all the experimental results obtained in investigations on the effect of surfaces on combustion processes. It seemed likely that the propagation of particular types of chain was, in certain cases, conditioned by the presence of suitable complexes present in the gas phases, and that these complexes were formed, at low temperatures at least, at the surfaces.

Dr. H. W. Thompson (*Oxford*) said : Dr. Adam has asked whether any convincing experimental methods have been used to show that reaction chains start on vessel surfaces. It may be worth while to mention the experiments of Alyea and Haber, in this connection, in which heated streams of hydrogen and oxygen were crossed at such pressures and temperatures that, according to measurements on the velocity of combination of these gases in quartz vessels, explosion should occur. No explosion was obtained in the absence of wall, but ignition immediately occurred when surfaces were introduced into the point of intersection of the gas streams, the surfaces being at lower temperatures than the mixing gases. These experiments and the conclusions to be derived from them are not to be regarded as entirely convincing. Similar experiments with carbon disulphide oxygen mixtures gave the same result, but here, too, there are objections to the method. The principle employed, however, seems interesting and capable of application.

Mr. A. Egerton (*Oxford*) said that Professor Bone's careful experiments on the slow combustion of ethane gave the result that no reaction products were detectable during the induction period, but this clearly showed that, since something must be happening, the quantities of initial products formed were small, and in all probability the action was going on at the surface, and products accumulating there.

Mr. C. N. Hinshelwood (*Oxford*), in reply, said : In some experiments which Mr. Thompson, Mr. Hadman and I are making on the combustion of carbon monoxide, we are hoping to separate the initial wall reaction and subsequent processes occurring in the gas. We have reason to believe that the first stage is a heterogeneous reaction $\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$ at the wall, followed by the propagation of chains in the gas phase. By comparing the rate of the water gas reaction in the absence of oxygen with the total rate of combustion of the carbon monoxide in the presence of oxygen, we expect to be able to find out something about the relative importance of the wall reaction and the homogeneous reaction.

⁸ Faraday Society Discussion, 24, 697, 1928.

PART II.—KINETICS AND ENERGETICS.

Professor H. S. Taylor (*Princeton*) said : Professor Benton's estimate of the magnitude of the possible third process (other than van der Waals' and activated adsorption) occurring with hydrogen on copper at 0° C. must represent an upper limit for this process which may, indeed, be negligibly small. Thus, if the value obtained at -78° C. for activated adsorption is not an equilibrium value then the value deduced at 0° C. for the same adsorption is too low, making the third process too important. The fact that gas adsorbed at -78° C. is desorbed on raising the temperature to 0° C. and is then re-adsorbed does not necessarily indicate that this re-adsorbed gas is not bound by activated adsorption. A consideration of the effect of heat of adsorption and activation energy of adsorption on the desorption of gas from a surface¹ shows that desorption on increase of temperature may be followed by readsorption on areas where favourable factors of heat and activation energy of adsorption are operative. The third process, whatever its ultimate magnitude may prove to be, is certainly not well described as solubility. Sievert's data, as the discussion on Ward's paper shows, are one order lower at least than the magnitudes here involved. Pending further investigation, it might be well to describe the third process as an activated diffusion as discussed theoretically by Lennard-Jones. The separation of activated adsorption and diffusion, if the latter really occur, is the central experimental problem of the subject at the present moment.

Professor A. Magnus (*Frankfurt*) said : An investigation into the adsorption of ethylene and hydrogen on gold powder and pyrophorous iron, obtained by heating the oxalate at a temperature not exceeding 300° C. and reducing traces of oxides by means of hydrogen at the same temperature, leads to precisely similar results to those depicted here. Whereas the isotherms for ethylene on gold are similar to those observed with charcoal, the adsorption on pyrophorous iron is relatively much higher at lower pressures, presumably owing to "activated" adsorption. Hydrogen, which is not adsorbed by pure charcoal at room temperature, is also but little adsorbed by gold. In contrast to this iron adsorbs it strongly. About 80 per cent. of the total quantity is taken up instantaneously; the remainder at a rate which is an exponential function of the time. The slow "adsorption," accordingly, would appear to represent a process of solution of hydrogen in iron.

Dr. C. Schuster (*Ludwigshafen*) said : In the case of the adsorption of hydrogen on active carbon we obtained two different forms of isotherm, according to whether we adsorbed at 0° or at 75° . Whilst the isotherm at 0° was a straight line—apart from the discontinuities which will be the subject of discussion relative to Professor Allmand's paper—the isotherm at 75° rises steeply from zero and then bends sharply. At lower pressures the adsorption of hydrogen is greater at 75° than at 0° . The quantity adsorbed is at 0° proportional to the pressure, but at 75° it is approximately proportional to the square root of the pressure. It would appear to be possible that in this case also we have activated adsorption. In any case, however, adsorbed ethylene is hydrogenated by adsorbed hydrogen just as much at 0° as at 75° , but the velocity at 0° is dependent on the hydrogen pressure whilst at 75° it depends on the square root of the pressure of the hydrogen.

¹ See Taylor, *Chem. Reviews*, Aug., 1931.

Professor A. J. Allmand (*London*) said: (1) Professor Taylor, in his introductory paper, states that conformity with the Langmuir equation necessarily means that the process is one of adsorption, as opposed to either solution or compound formation. This is surely incorrect, as was demonstrated some years back by Hitchcock.² If the gas B form a compound AB with the substrate A, this compound dissolving in the excess of A to form a homogeneous phase containing negligible amounts of uncombined B, a phase moreover which behaves as an ideal solution, then the following equation holds

$$[AB] = \frac{([A] + [AB])k_1Kp_B}{1 + k_1Kp_B}$$

where $K = [AB]/k_1p_B[A]$ and $k_1p_B = [B]$. This expression is analogous in every detail with the Langmuir equation

$$\frac{x}{m} = \frac{k'bp}{1 + bp},$$

and, in view of the work of Davisson and Germer and of Rupp, which indicates that hydrogen adsorbed by nickel may enter the lattice, it seems that the point is one which should be kept in mind.

(2) I would be interested to know if there is imagined to be any connection between activated adsorption and the slow rate at which hydrogen over-voltage reaches its maximum value with cathodes of such metals as Fe, Ni, Pt, Cu, Au, etc. As is known, the process in question can easily take hours to complete at room temperature. The majority of the metals concerned tend to have high melting-points and low final hydrogen over-voltages, to dissolve hydrogen gas comparatively readily and to exhibit anodic passivity. The decay curve following on the cessation of cathodic polarisation, and the recovery curve following on a brief anodic polarisation are indicative of processes far more rapid than the slow over-voltage rise. An originally "plane" cathode surface becomes roughened during the course of electrolysis, but any "solution" of hydrogen is certainly confined to the surface layers, as very light abrasion suffices to reduce the potential of cathodically polarised nickel to that of untreated metal. A preliminary pickling with acid will cause iron to assume immediately a high over-voltage value when cathodically polarised.

The interesting point is that, *if* the slow process is one of activated adsorption, it can hardly be bound up with the dissociation $H_2 \rightarrow 2H$, as H atoms are presumably the primary product of electrolysis.

(3) I would suggest that, in some cases, the process which requires activation energy may be the displacement by the sorbate of residual gas adhering to the adsorbing surface.³ Thus, in the course of experiments carried out by Dr. Chaplin in the King's College laboratory, slow adsorption of CCl_4 vapour on charcoal was found to be accompanied by slow evolution from the charcoal surface of oxygen in the form of oxides of carbon, and we concluded that these facts were interconnected. The difficulty of removing the last traces of gas from the surface of a sorbent and the effects of such traces on adsorption phenomena have been emphasised from one point of view or another by several contributors to this discussion (Rideal; Bonhoeffer and Farkas; Frankenburg; Benton; Ubbelohde; Maxted and Hassid; Roberts). Taken in conjunction with our own results, this appears suggestive.

² *J. Amer. Chem. Soc.*, **48**, 2870, 1926.

³ See *Proc. Roy. Soc.*, **132 A**, 474, 1931.

The **President** referred to the difficulties experienced by Dr. Shields (Dr. Ludwig Mond's assistant) when working in Sir Wm. Ramsay's laboratory on the occlusion of oxygen and hydrogen in platinum and palladium black, and later by Dr. Meyer Wilderman working on the chemical action of light. They had found difficulty in removing the adsorbed film of gases from the glass vessels and tubing they employed, and had found it necessary to proceed exhausting with tubes raised to a red heat in order to obtain consistent results. He also referred to thermoelectric effects and to Professor Spring's work at Liege on the intergrowth of polished surfaces of zinc and copper as throwing light on the conditions for acting on a metallic surface.

Dr. A. F. H. Ward (*Manchester*) said: During this discussion it has been suggested that the hydrogen taken up slowly by copper cannot be in solution as the figures obtained by Sieverts for solubility are very much smaller. It is essential to remember, however, that diffusion of the gas into the metal and resulting solution may occur in two ways—either along grain boundaries and planes of weakness or through the lattice. The large amounts of hydrogen in solution at ordinary temperatures are almost certainly concentrated along the Smekal cracks. At the much higher temperatures at which Sieverts' solubility measurements were made these cracks would be greatly diminished owing to the sintering of the metal so that the difference in the structure of the copper and the nature of the solution would account for the different results obtained. Whether this phenomenon can strictly be called solution is merely a matter of nomenclature. Objections have been raised that a solution should be homogeneous. A limit can be reached when any system ceases to be homogeneous by considering progressively smaller amounts. In this case the limit is reached for particles of the order of the grain size between Smekal cracks — 10^{-4} cm.

Mr. C. N. Hinshelwood (*Oxford*) said: The energy of activation of adsorption is determined by measuring the temperature coefficient of the rate of a slow adsorption process. It seems to me that a distinction should be drawn between those temperature effects which really depend upon activation of the molecules, and those which depend simply upon changes with temperature in the state of the solid adsorbent. The latter are indistinguishable experimentally from the former, but do not really signify much in connection with the nature of the adsorption process. The structure of solids is well known to be very imperfect: there is a large internal surface ("Smekal cracks," etc.) some of which may be difficultly accessible at one temperature and much more easily accessible at a higher temperature. The size of these cracks at any given temperature will probably be distributed about a mean according to a Gauss error curve: the modulus of this will vary with temperature—possibly more or less linearly—and the proportion of particularly easily penetrable cracks may quite easily vary more or less exponentially with temperature over a certain range, giving the illusion of an activation factor. Some years ago Mr. Bowen and I tried to measure the heat of activation of processes involving the decomposition of solid substances: we found the actual temperature coefficients to depend so much on changes in the structure of the solid that they meant very little. The whole complex question of solid structures and their variability is discussed in Sir George Beilby's book on the "Aggregation and Flow of Solids," the importance of which in connection with these problems I should like to call attention to.

Professor T. M. Lowry (*Cambridge*) said that it was important to distinguish between the solubility in an undisturbed crystal and in the amorphous material of the slip-planes of a strained or unannealed crystal. The former was comparable with the solubility in the liquid and might be enormously larger.

Professor R. H. Fowler (*Cambridge*) said: It appears to me that we are talking rather freely about the diffusion of gas atoms *into the lattice* of a metal crystal (true solution) at room temperatures, or temperatures not much higher, without enquiring whether such a process actually occurs. The experiments of Rupp and of Davisson and Germer on the diffraction of electrons have been cited; they claim to have found reflections under certain conditions of the surface which must be interpreted as half-order Bragg reflections, indicating that something has happened which makes alternate planes of atoms in the lattice of different scattering efficiency without altering the spacing. While the experiments of Rupp on the effect of hydrogen on the reflections from nickel (111 face) and from iron or molybdenum (110 face) may almost certainly be thus interpreted, G. P. Thomson⁴ has found no such abnormal reflections at all with crystals of copper and silver, and has shown that many of the "abnormal" reflections of other experimenters may not need any such alteration of the lattice structure for their explanation. This is not to say that metal *lattices* do not dissolve gases, but that electron diffraction does not provide as yet much good evidence.

On the other side there is the convincing evidence of von Hevesy's experiments on the diffusion of radioactive lead into lead that, at temperatures not near the melting-point, diffusion into the *lattice* effectively does not occur at all, the diffusion actually observed with polycrystalline lead taking place entirely along the grain boundaries. Thus, as one would expect, the process of diffusion into the lattice must be a highly specific one, depending markedly on the metal, the gas and the temperature.

Dr. J. T. Randall (*London*) said: In support of Professor Fowler's remarks that the idea of true solution of a gas in a lattice is to be regarded with suspicion, unless there is definite X-ray evidence to the contrary, the following may be of interest. In order for the impinging gas atoms to penetrate the lattice the amplitudes of vibration of some of its atoms must exceed the diameter of the colliding atom or molecule. Now, the mean amplitude of vibration of atoms in a lattice is known only with certainty from the work of James and Firth⁵ on NaCl where the figures are 0.2 Å. and 0.58 Å. respectively at 290° K. and 900° K. Impinging molecules would need to be of very small diameters to penetrate very far into this lattice. On the other hand, some crystals are not in close-packed arrangement at room temperatures, and it is fairly easy to see that in the case of beryl, for instance, molecules might easily penetrate the lattice. Even body-centred metallic lattices are, however, fairly closely packed and copper has, of course, the cubic close packing arrangement.

Dr. F. J. Wilkins (*London*), in reply to Professor Fowler's question asking for experimental evidence relating to lattice diffusion, said: I have shown⁶ that Feitknecht's measurements of the rate of oxidation of copper at temperatures above 800° C. are satisfied by the equation $x = kt + c$ where x is the amount of oxide formed at time t and k and c

⁴ *Proc. Roy. Soc.*, **133A**, 1, 1931.

⁵ *Ibid.*, **117**, 62, 1927.

⁶ Wilkins, *Z. Elektrochem.*, **35**, 500, 1929.

are constants. This implies that the diffusion coefficient of the oxide film for oxygen remains unchanged during the oxidation. Feitknecht, however, showed that during the oxidation the grain size of the oxide film increased considerably and we are therefore driven to the conclusion that the diffusion of oxygen through the oxide film is at these temperatures preponderatingly a lattice diffusion.

Dr. N. K. Adam (*London*), in reply to Dr. Wilkins, said: It seems possible that, although the number of inter-crystalline channels is probably reduced by sintering, their individual size increases; this might account for the apparent "diffusion" rate through the metal being constant. Are there reliable data on diffusion of gases through *single* crystals of metals? It seems very important to distinguish between bulk diffusion through an uninterrupted crystalline space lattice and creeping, or surface diffusion, along cracks between small crystalline grains. It is well known that the atoms in some metallic lattices become mobile below the melting-point, and it would be easy to understand bulk diffusion through metals occurring when the atoms of the metal itself are moving. It is more difficult to understand bulk diffusion at lower temperatures where there are no translatory motions of the atoms. One is tempted to conclude, from the fact that the diffusion rates observed by Sieverts are so small, when the metals are well annealed, that there would be practically no diffusion in the absence of any cracks.

Dr. F. J. Wilkins (*London*) said further: Dr. Adam's suggestion that sintering while causing a decrease in the number of grain boundaries also causes an increase in their average cross-section may be true, but it can hardly account for the experimental results, for they demand that the decrease in the total cross-sectional area of the grain boundaries due to the decrease in the number of the grains should be exactly balanced by the increase due to the supposed increase in the average cross-sectional area of the grain boundaries.

Dr. N. K. Adam replied: I daresay Dr. Wilkins' suggestion that there is a case of genuine lattice diffusion here is correct, as in this instance the temperature was only about 300° below the melting-point of cuprous oxide, so that there may have been some mobility of the atoms in the lattice.

Professor E. K. Rideal (*Cambridge*) said that he was struck by the low value for the heat of dissociation of the superficial hydride as calculated from the pressure temperature curve. How would this value be explained if true equilibrium existed over the range? He would like to ask another question. We define as a unique point the melting-point of a three-dimensional solid; can we define this equally well for a two-dimensional chemi-adsorbed film? A closer analysis of that problem indicates that an increasing number of molecules acquire energy necessary for liberation as the temperature rises; does structure collapse set in at a melting-point? The process of fusion resulting in the primary formation of small aggregates and then of single molecules takes place over a small but finite temperature range; two-dimensional fusion of an assemblage of presumably slightly different types of adsorbed molecules should take place over a temperature range.

Dr. L. Tronstad (*Trondheim*): The question of the *solubility* of gases in the metal lattice has been raised several times during the discussion, for example by Professor Fowler, but some uncertainty seems to prevail with respect to this point. At low temperatures the solubility is usually very low, and might therefore be neglected in

comparison with the adsorbed quantity of gas. At *higher* temperatures, however, where the "activated" adsorption should be more liable to take place, the solubility is more pronounced, and it is therefore important to pay proper attention to this solubility.

The fundamental work of Sieverts and collaborators has often been referred to in the discussion; some recent work, however, seems to have been disregarded. I should especially like to call attention to work carried out in Stockholm by Borelius and collaborators regarding the solubility (and diffusion) of hydrogen in metals, in which the problem is given a rather complete thermodynamical treatment.⁷ By means of X-rays and conductometrical measurements, they have also tentatively given the *equilibrium diagram* for the system hydrogen-palladium (see also G. Hägg below). The work of A. Coehn and collaborators⁸ may also be of some interest. This work deals with the solubility and diffusion of electrolytically deposited hydrogen in a palladium wire. Two very interesting methods, a potentiometric and a "photograph," were employed. (The photographic method depends on the fact, that hydrogen on palladium reacts with oxygen to form the peroxide of hydrogen, which produces a blackening of the usual bromide paper.) The experiments carried out seem to indicate the presence of hydrogen ions or protons in the lattice. However, no precautions were taken to prevent a surface migration of adsorbed hydrogen during the experiments, and therefore one should expect the results to be somewhat uncertain. Nevertheless, it seems important to the question of adsorption, to carry out new experiments, both with the system palladium-hydrogen and other systems, under more *definite conditions* (for instance with tempered single crystal wires and precautions to prevent surface migration) in order to determine the diffusion velocity of hydrogen in the metal lattice. Under such definite conditions it would also be useful to make conductometric determinations of the solubility.

The question of the solubility of nitrogen in metals is treated in the fundamental work of A. Fry,⁹ and regarded highly by metallurgists (surface hardening of steel). In this respect, I should like to mention important X-ray work carried out recently in Stockholm by G. Hägg.¹⁰ Hägg has also examined hydrogen-metal systems. Powdered samples of the transition elements (iron, manganese, titanium, etc.) were examined by means of the focusing camera, when exposed to nitrogen or ammonia at different temperatures and pressures, and the lattice structure of the solid solution or solid compound formed was determined. In some cases, even the equilibrium diagram could be plotted. Under certain conditions, the equilibrium was reached in rather short time. The amount of nitrogen taken up by the different metals varied within a wide range with the temperature and pressure. For instance, scandium, titanium, and vanadium took up a maximum content of 50 atoms per cent. of nitrogen quite easily. (The nitrides of scandium and titanium could be melted at about 2000° C., the dissociation pressure is therefore low.) Manganese took up a maximum content of about 40 atoms per cent., and the dissociation pressure was equal to 1 atm. at about 500° C. The solubility of nitrogen in α -iron was rather low compared

⁷ G. Borelius, *Ann. Physik*, **83**, 121, 1927; J. O. Linde and G. Borelius, *ibid.*, **84**, 747, 1927.

⁸ A. Coehn, *Z. Elektrochem.*, **35**, 676, 1929.

⁹ A. Fry, *Stahl und Eisen*, **43**, 1271, 1923.

¹⁰ G. Hägg, *Z. physikal. Chem.*, **6B**, 221, 1930; **7B**, 339, 1930; **9B**, 455, 1930; **11B**, 433, 1931; **12B**, 33, 1931.

with the metals mentioned. In this case the dissociation pressure was very high even at low temperatures; at the same time the diffusion velocity was also slower than in the other metals. However, by using ammonia, a nitride of iron with 33 atoms per cent. of nitrogen, although unstable, could be obtained very rapidly at 300° C. (corresponding to 11.2 per cent. nitrogen by weight!). The explanation for this fact is, that the diffusion velocity of ammonia in the iron lattice is, as may be expected, much higher than of nitrogen, and that the velocity of formation of iron nitride from ammonia and iron is much larger than the velocity of decomposition of the nitride formed. The solubility of nitrogen in nickel and cobalt lattices was less than in the iron lattice, and with ammonia no nitrides could be obtained. The reason for the different behaviours of metals in presence of nitrogen (and also other gases) lies both in the difference in the interacting atomic forces, and in the different dimensions of the lattice interspaces.

Professor Benton in his paper and in the discussion has pointed out, that a "solution" did not take place in the case of iron, nickel or cobalt and nitrogen. This fact can easily be understood in the light of the experiments mentioned above (solubility of nitrogen in iron low, and in nickel and cobalt still lower). It might, however, be of interest to the question of the effect of solubility to carry out experiments under definite conditions with, for example, titanium, vanadium or even manganese and nitrogen, as these metals show a pronounced nitrogen solubility. Also, the system iron-ammonia ought to be examined.

Professor R. H. Fowler (*Cambridge*) said: The evidence cited by Dr. Tronstad is just exactly the type of evidence we require. He told us how X-ray analysis has shown when nitrogen can be inserted into the lattice of certain metals of the iron transition group. It seems to me that for the understanding of adsorption, especially what is known as activated adsorption, every effort should be made to use this type of evidence wherever it is or can be made applicable, and not to speculate on solution without, if possible, direct experimental control.

With regard to the possibility of *melting in two dimensions*, Professor Fowler said, a contrast has been drawn between a change of state of the adsorbed surface atoms from bound states to free states (two-dimensional gas states) and an onset of the process of hopping from one valley of potential energy to another due to thermal agitation in the underlying solid. I think this contrast is specious. Both descriptions are quite legitimate, but they describe the same event merely in slightly different language. From the points of view of an adsorbed atom the solid surface is a set of bumps and hollows of potential energy of which the following figure is a one-dimensional section.

C

There are states of low energy such as at A in each hollow for which the surrounding mountains are so high that the atom practically never penetrates to the next hollow. Such states are bound states. There are also states of considerably higher energy, as C, in which the atom moves practically freely over the surface. There are states between of every intermediate grade of freedom. Raising the temperature means increasing the number of adsorbed atoms in the free states at the expense of those bound, according to Boltzmann's distribution law. As the

majority will pass over from bound to free states when kT is nearly equal to the height of the mountain peaks above the lowest levels, this process represents the *melting* of the adsorbed film and seems to be closely analogous to the process of melting of solids.

Instead, however, of using the ideas of stationary states of the whole surface one can concentrate instead on the properties of a single valley and the behaviour of the atom there, and regard the presence of neighbouring valleys as a perturbation. Raising the temperature, and therefore the energy of the atom in its valley, may then be said to stimulate a process of activated hopping from one valley to another over or through the tops of the mountains. In one picture one takes as fundamental the stationary states for the atom in the *whole* surface field, in the other for the atom in a single valley with perturbations. That is the sole difference—one of description and a matter of taste at that—not corresponding to any physical difference at all.

On the question whether *adsorption of caesium on tungsten is activated*, Professor Fowler said it has been mentioned in the discussion that the adsorption of Cs on W is or may be activated; adsorbed Cs is certainly mobile and this would conflict with certain views of the nature of activated adsorption. Now whatever the facts may be, it seems clear from any existing theoretical point of view that the adsorption of Cs on W is in no sense activated. It is of course *ionic*. Any Cs atom brought near any metal whose work function exceeds its very low ionisation potential, can in general only stay there a very short time before losing its electron after which it will be securely bound to the metal by the image forces. Such adsorption is the strict analogue of a *polar* molecular binding such as NaCl, and it must obviously be expected to be mobile on the surface, but no energy of activation is needed to enable the transfer of the electron to take place. It can occur freely by the "tunnel effect" as soon as the Cs atom comes within 10^{-7} cm. or so of the surface of the metal.

Mr. A. R. Ubbelohde (*Oxford*) said with regard to the general introduction by H. S. Taylor¹¹: It is clear that the activation energy of 13,500 cal. in the case cited by the author is necessary, but not sufficient for activated adsorption to take place. One explanation of the fact that the rate of adsorption is much smaller than would be expected from the number of activated molecules striking the surface is given in the above communication. Alternatively, we may suppose that the process involving 13,500 cal. can only take place with molecules striking a few active points in the surface. The total adsorption is not limited by the small number of these points, since the molecules once adsorbed may migrate over the surface, but the abnormally slow rate of adsorption in spite of the *low* activation energy is explained (*cf.* the data of F. Kingman, and on Pd/H₂ in this discussion).

Professor A. F. Benton (*Virginia*), in reply, said: I agree with Professor Taylor that it is possible to imagine a distribution of heat and activation energy of adsorption such that gas adsorbed at one temperature could be partly evolved at a higher temperature, followed by re-adsorption on other areas. Even if it be granted that factors favouring this situation commonly occur in the numerous cases cited in my paper, they will not account for the fact that in certain ranges of volume gas is *taken up much more rapidly* at a lower temperature than at a higher. Thus with copper and hydrogen a comparison of the rates at -78.5 and 0° , measured at approximately equal pressures and in both cases far

¹¹ This vol., p. 157.

from final equilibrium, shows that while the sorption of the sixth c.c. was much more rapid at the higher temperature, the sorption of the next 0.5 c.c. required 408 minutes at 0°, but only 34 minutes at -78.5°. The very slow process at 0° must be a different process from the activated adsorption at -78.5°. It is this process, thus sharply distinguished experimentally, which we have "provisionally ascribed to solution." I do not agree that the values obtained represent an upper limit, but rather a lower limit for this process. Professor Taylor's views on the surface distribution of the activation energy of desorption are based on the meagre data available for the variation of heats and activation energies of adsorption as the extent of adsorption increases. If activated adsorption is frequently accompanied by a "solution" process, the heat of the total sorption, either observed or calculated from isotherms, will be composite of the heats of the two separate processes, as will also the activation energy. Consequently, it must be concluded that the surface distribution of these quantities for activated adsorption alone is unknown in such cases at the present time. It is significant that Ward,¹² using a technique which eliminated effects due to "solution," found no variation of the heat of activated adsorption of hydrogen on copper at 0°.

In the discussion objections have been raised to the tentative use of the word "solution" to classify the process in question, on the ground that the values obtained are much greater than the solubilities found by Sieverts. It seems worth mentioning that Sieverts determined the solubility of hydrogen in nickel only above 218°, and in copper and iron only above 400°, and that even at these temperatures no convincing evidence was given to show that equilibrium was attained. It is possible that the "true" solubilities would be greater at lower temperatures, as Steacie and Johnson¹³ found to be the case in the system, silver-oxygen. Further, as Dr. Adam points out, we do not know that Sieverts' data refer to lattice solubility; if they refer to intergranular diffusion, one would expect much larger values for metals prepared by reduction at low temperatures. In the discussion it has apparently been taken for granted that the crystalline surfaces of such metals are interlaced with Smekal cracks roughly 10^{-4} cm. apart. Such cracks would not be an important factor if the average size of the crystals is less than this value, as seems probable from such studies as those of Wyckoff and Crittenden,¹⁴ and of Schmidt.¹⁵ I think our experiments are to be regarded as showing that a slow process other than activated adsorption commonly occurs even at moderate temperatures, but the exact nature of this process is for future investigation to decide.

Professor Fowler, in his remarks on the adsorption of caesium by tungsten, and also Mr. Goodeve, raise an important point regarding the significance of the word "activated" in reference to adsorption. If by this term one means merely a process which is not instantaneous and which may, therefore, be said to require an activation energy, the adsorption of caesium is certainly not of the activated type. It is equally clear that it is not of the van der Waals' type. It can be considered an activated adsorption in the sense that the caesium atom is activated to the point of ionisation. In spite of the recent emphasis on rate of adsorption, many workers in this field will doubtless continue to regard as "activated" or "chemical" adsorption all those cases in

¹² *Proc. Roy. Soc.*, **133A**, 506, 522, 1931.

¹³ *Ibid.*, **112A**, 542, 1926.

¹⁴ *J. Am. Chem. Soc.*, **47**, 2866, 1925.

¹⁵ *Z. physik. Chem.*, **118**, 193, 1925.

which the configuration of the adsorbed atom or molecule is fundamentally altered. I cannot agree with Mr. Goodeve that a molecule held by activated adsorption is necessarily at a lower energy level than when physically adsorbed. Data on heats of adsorption leave no doubt that the *complex, adsorbent-adsorbate*, is at a lower energy level, but the activity or free energy of the chemically adsorbed molecules as such (if we can speak of such a quantity) is very frequently increased, as we know from the phenomena of surface catalysis.

Mr. C. F. Goodeve (*London*) said: I trust that the term "activated adsorption" is only a temporary one until more is known about the phenomenon with which it has been associated. It may be justified to use the term to describe the *process* of adsorption, but many speakers have employed the words to describe the *state* of the adsorbed layer. Such a use leads to confusion. The word "activated" has been used almost universally to describe a condition of higher energy than the normal, while there seems little doubt that a molecule following the so-called "activated" adsorption process is at a very much lower energy level. Strictly speaking, the term "post-activation adsorption" should be used.

Professor A. F. Benton (*Virginia*) said: The extensive studies of discontinuities in adsorption, carried on during the past four years by Dr. White,¹⁶ have led to a number of general conclusions. Discontinuities have been found only in physical adsorption. They have been found in all cases of physical adsorption where a sufficiently detailed investigation was made. In any given case, the volumes corresponding to successive steps are approximately equal. The pressure intervals display less regularity, but show a general tendency to increase with increasing pressure and with increasing temperature. Foreign gases, even in relatively large quantities, exert little effect. Sintering the adsorbent results in a decrease in the volume interval between steps. Since the individual crystals and even the poly-crystalline grains are extremely small, it is obvious that the observed steps of 0.2 to 0.3 c.c. cannot be attributed to phenomena occurring at a single crystal or grain. It must be concluded that when a step occurs, a very large number of crystals, probably all of them, each take up a quantity of gas suddenly and *practically simultaneously*. This requirement leads logically to the view that the cause of the observed discontinuities is to be found in those properties of the crystals which are identical for all. On the basis of available information a hypothesis was advanced, according to which the discontinuities observed with crystalline adsorbents represent the formation of successive rows of adsorbed molecules parallel to the edges of the crystals. The known facts were shown to be in agreement with this view.

Professor H. S. Taylor (*Princeton*) said: It is worthy of remark that both in the contributions of Professors Allmand and Benton the discontinuities in the isotherms seem to be confined to the cases in which we are dealing with van der Waals' adsorption. The breaks do not appear in the cases of activated adsorption. This suggests that the discontinuities may be associated with the mobility of the molecules in the surface when held by van der Waals' forces. It suggests that there may be a very much diminished mobility of gases held to the surface by the forces operative in activated adsorption, a point of view also discussed in the opening address. On the other hand, the discovery of

¹⁶ Benton and White, *J. Am. Chem. Soc.*, **52**, 2325, 1930; **53**, 2807, 3301, 1931.

discontinuities in an activated adsorption isotherm may involve the use of a very much longer time scale than has hitherto been used owing to the time factor in activated adsorption. The search for discontinuities in activated adsorption must undoubtedly be made in the highest temperature ranges in order to minimise the time required for the work. Such isotherms of activated adsorption as show reasonable reversibility on raising and lowering the pressure would be best suited to this purpose.

Dr. C. Schuster (*Ludwigshafen*) said, with reference to Professor Allmand's paper, that they had found an isotherm with hydrogen at 0° on active carbon which exhibited quite definite discontinuities; according to the communication of Professor Benton these are in good agreement with his observations (see Fig. 1).

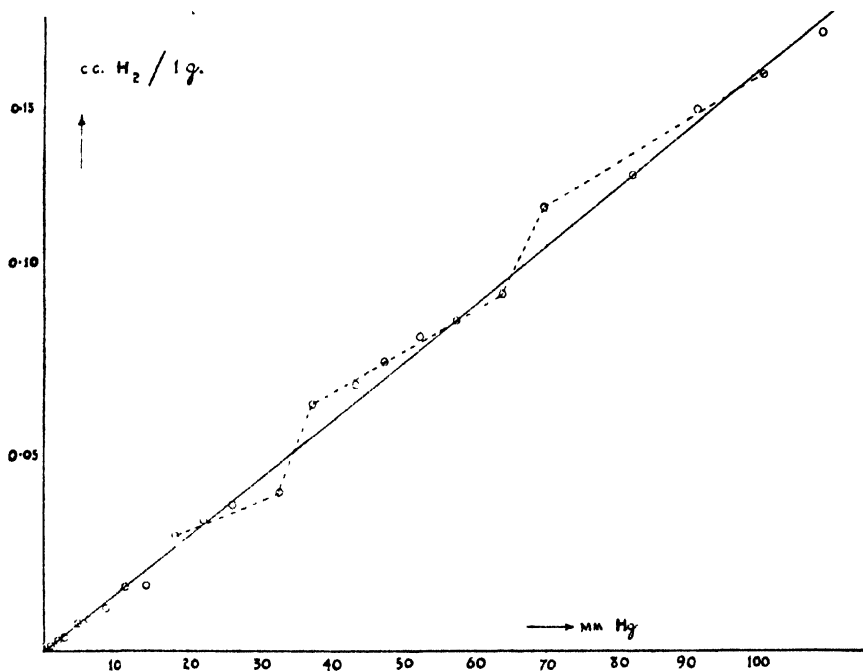


FIG. 1.

Dr. K. G. Emeléus (*Belfast*) said: If the discontinuities in adsorption are associated with abrupt changes, it should be possible to demonstrate them by placing the system between the plates of a suitable condenser connected to an amplifier and loud-speaker or galvanometer, and if this experiment were successful, possibly also to obtain information about the nature of the changes, as in the Barkhausen magnetic phenomenon.

Dr. N. K. Adam (*London*) said: It is rather difficult to accept Professor Benton's general statement that "physical adsorption appears to be characterised by a discontinuous increase of adsorption with pressure." The "physical," or Van der Waals' forces required to give such a result on an ideal plane surface would be of an extraordinary character. Surely measurements of the adsorption of a more or less perfect gas on a plane, impermeable surface free from cracks would not show discontinuities? It seems more likely that the discontinuities

observed are due to the very complex structure of the charcoal and metallic adsorbents used.

Were the metals in a compact condition, or in the spongy, porous state called by Beilby the "open formation," which is often produced by the action of gases on metals far below their melting-points?

It seems possible, as Dr. Wilkins suggested to me recently, that the discontinuities are due to the adsorbed gas accumulating in cracks, splitting some of them open further at a definite pressure. When this occurs, fresh adsorbing surfaces would be suddenly exposed to the gas and a discontinuity should be observed in the isotherm. This could be tested, as one would expect such a splitting action (the adsorbed layers acting as minute wedges) to be at least partly irreversible, so that the original form of the isotherm would be altered during a second adsorption after desorption, *i.e.*, there should be a good deal of "hysteresis" in the adsorption isotherms.

It might not be difficult to make simultaneous measurements of adsorption and of the expansion of a stick of gas carbon, or some other porous yet coherent solid, by affixing a flat plate to one end of the stick and using this plate as one end of an interferometer or a Whiddington ultra-micrometer.

Dr. F. J. Wilkins (*London*) said: Dr. Adam has already mentioned a suggestion which I had put forward as a possible explanation of the discontinuous adsorption isotherms observed by Professors Allmand and Benton. I do not agree, however, that the theory implies irreversibility. The reason will become clear perhaps from the following statement. It is known that charcoal expands when gases are adsorbed by it. Whatever may be the reason for this expansion it is evident that one consequence of it is an increase in the intergranular distance. The first amounts of gas adsorbed will go to the outermost set of grains and begin to increase the distance separating them. This increase will proceed for a given pair of grains until the intergranular grain distance is sufficiently large to permit of the passage of adsorbed molecules. When this occurs a further area of charcoal becomes available for adsorption and one would expect a discontinuous adsorption isotherm. There is no obvious reason for supposing such a process to be irreversible. The action of adsorbed vapours in removing the last traces of permanent gases from charcoal is perhaps to be attributed to the widening of the intergranular spaces.

Mr. A. R. Ubbelohde (*Oxford*) said: A possible explanation of discontinuities in adsorption isotherms is given by Ubbelohde and Egerton.¹⁷ I would like to ask Professor Allmand whether the silica on which he and Dr. Burrage observed discontinuities was crystalline or not.

Professor A. F. Benton (*Virginia*) said: In reply to Dr. Adam's question, the metals with which discontinuities were observed were in the finely-divided state obtained by reduction at relatively low temperatures. Further details are given in the paper presented in this Discussion. There was no evidence of irreversibility in the discontinuities.

The possible explanation of discontinuities advanced by Dr. Wilkins seems to me very difficult to reconcile with existing facts. It is not clear on this basis why there should be more than one, or at most a small number, of discontinuities, nor why the volume intervals between steps should show the striking regularities which have been observed. Finally,

¹⁷ *Proc. Roy. Soc.*, **134A**, 512, 1931.

the sudden increase of the intergranular distance would not be expected to occur at identically the same pressure for every granule. It has previously been emphasised that the steps would represent immeasurably small volume differences unless all or most of the granules are simultaneously involved.

Professor A. J. Allmand, in reply, said: In reply to Professor Benton, I do not agree that the time has yet arrived for putting forward explicit theories to explain the cause of discontinuities in sorption phenomena. Although I admit to being impressed by the degree of concordance between his own observations and calculations, I think that, working with any particular sorbent, an intensive investigation of the nature of its surface structure, combined with a study of the effects of temperature and of variation in nature of sorbate, is a desirable preliminary to any theorising. There is no need to imagine that the detailed cause will be the same in such different systems as copper— H_2 , silica gel— H_2O , charcoal— CCl_4 . Adsorption depending on the presence of "active centres,"¹⁸ or, in particular, starting from crystal edges, or condensation taking place in capillary pores or in "molecular gaps" or in Smekal cracks or along inter-granular boundaries—each may be responsible for breaks in certain cases but not in others.

I think Professor Benton rather exaggerates the uniformity of the quantity increments between breaks as shown in his own published work, just as we ourselves were inclined originally to overestimate the concordance observed between our different characteristic pressure values. As stated in our contribution, these quantity increments, using water vapour, are far greater at intermediate than at high and low pressures, in agreement, of course, with the general form of water vapour isothermals. We agree¹⁹ that the actual *number* of breaks found within a moderate pressure range raises certain difficulties, and will be of importance when theorising.

The data of Dr. Schuster are very similar in general nature to those observed by us in other systems. I am much obliged to Dr. Emeléus for his suggestion and shall hope to try it out.

In reply to Dr. Adam, I may say that, in the two cases where such experiments have been done, *viz.*, CCl_4 on charcoal (*loc. cit.*, Fig. 4, p. 617) and CO_2 on charcoal (Fig. 1 of present communication), isothermals with discontinuous structure have been found to be reproducible and reversible. I agree with him that breaks would not be anticipated on a truly uniform surface. His suggestion, made to me in a somewhat modified form by Dr. Wilkins, that the phenomena are connected with the presence of Smekal cracks or similar discontinuities in the structure of the sorbent, and might perhaps be correlated with the expansion known to take place during adsorption in certain cases, is one of considerable interest.

In reply to Mr. Ubbelohde, the silica on which Dr. Burrage observed discontinuities was a specimen of commercial silica gel.

Dr. W. Frankenburger (*Ludwigshafen a. Rh.*) said: The working hypothesis put forward by Allmand and Chaplin²⁰ appears to us well worthy of consideration as an explanation of many experimental observations on "activated adsorption," particularly those dealing with charcoal. It cannot, however, apply to the cases we have studied.

¹⁸ Regarded by us quite generally as regions of high adsorption potential (*Proc. Roy. Soc.*, **129A**, 261, 1930; **130**, 627, 1931).

¹⁹ *Proc. Roy. Soc.*, **130A**, 630, 1931.

²⁰ This vol., p. 223.

This follows from the fact that the anomalous increase in the amount of adsorbed substance (H_2 and N_2) is noticeably greater in the case of purified tungsten powder preparations (particularly those which are well and carefully reduced) than it is in the case of powders of a lower degree of purity, in which, indeed, this effect is considerably less noticeable. Activated adsorption is evidenced to so much the greater extent, and within so much the lower temperature range, as the powder has been the more carefully freed from oxide; at the same time the removal of the last, obstinately retained, traces of oxygen effects a particularly strong increase in the "activated adsorption." Thus the behaviour is quite contrary to what would be expected according to the Allmand hypothesis and the *experimentum crucis* he has put forward. Moreover, we may indeed conclude from the fact of the reproducibility of experiments carried out with one and the same powder, that the adsorptive condition of tungsten powder does not alter after somewhat numerous successive measurements, even at increasing temperature. According to Allmand we should, however, expect that after a single "displacement" of the foreign gas (oxygen) by the adsorption gas (hydrogen) the adsorbent would show in a further experiment a notably higher absorptive capability (rather than the phenomenon of "activated adsorption" to a lesser extent) by reason of its greater freedom from oxygen.

Thus we deduce from our experiments that reactive spots of the tungsten surface which are *freely exposed owing to careful purification*, and protected from foreign gas (oxygen), are to be considered as centres of "activated adsorption." With less efficient purification the evidence of these tungsten spots is bound up with their oxidation; the influence of polluting foreign gas on the phenomenon of "activated adsorption," in the system we have studied, runs thus quite contrary to the views of Allmand and Chaplin.

Dr. A. F. H. Ward (*Manchester*) (*communicated*): The suggestion that the removal of impurities from the surface is the slow activated process in the adsorption of vapours on charcoal gives a very neat explanation of the phenomenon. A factor which would give a useful test to the theory is the behaviour on desorption. On a perfectly clean surface, if diffusion effects did not occur, both the adsorption and desorption of the vapour should be instantaneous. Desorption should still be practically instantaneous if impurities are there which hinder adsorption, though in this case the vapour molecules which are on those active surface atoms which previously held the oxygen might be supposed to be removed more slowly. These, however, are assumed to be few compared with the number of vapour molecules which they can prevent from being adsorbed, so the amount of the slow desorption should either be zero or small compared with the slow adsorption.

For the adsorption of hydrogen on copper, it is doubtful whether the theory of Allmand and Chaplin would give a complete explanation, for in this case after the instantaneous reversible desorption there was a slow desorption comparable in amount with the slow adsorption (though at low temperatures, before the interior of the copper was saturated, the slow desorption soon changed to a slow adsorption as more gas diffused to the interior). The crucial test suggested by Allmand and Chaplin was actually carried out in this work. The most probable surface impurity, oxygen, was removed by treatment with hydrogen at higher temperatures than those of the adsorption experiments, yet nevertheless the slow adsorption occurred.

Dr. H. K. Cameron (*London*) (*communicated*): Mr. Burrage²¹ has raised a question which is becoming as increasingly important as it is disconcerting to those who are interested in this field of work. While there can be no doubt that his criticisms are in general justified, the opportunity might have been taken in such a discussion as this to elaborate from existing experience some standard and more reliable methods for preparing and activating surfaces.

The methods used must be as numerous as the publications in this field, and each worker has hitherto decided his own procedure.

With metal surfaces as adsorbents it is clear that it is much more difficult to remove all traces of adsorbed material than was at one time thought. Work on thermionic emission²² in particular has demonstrated this. Such possibilities as surface mobility and diffusion along grain boundaries, or Smekal cracks, and lattice penetration seem likely to lead to some measure of irreversibility of adsorption; this will certainly be so unless the temperature is taken higher than may be convenient for the preservation of the initial surface.

Glasses provide unsuitable surfaces for such work, their adsorptive properties depending largely on the previous history and nature of the material, which is undergoing a continuous change.

As to charcoal, it is recognised as a commercial adsorbent of great value, and it is consequently used repeatedly in pure research. Different treatments are undoubtedly advantageous according to the particular adsorption reaction to be studied, but it should be recognised as of first importance in all published data to state:—

1. The exact source of the material. Whenever possible the origin of the tree, sugar, etc., should be given; in the case of a patent activated carbon, the manufacturer and date of purchase.

2. The subsequent history of the specimen, especially as regards ageing in bottle or in air.

3. The ash content and precautions taken to reduce it. This important factor is too frequently overlooked.

4. The screening analysis; and

5. The pre-treatment in the particular experiment, involving cleaning or activation processes.

In respect of this last point, it is now almost certain, as Mr. Burrage points out, that evacuating at high temperatures is in itself insufficient to clean up a surface; at best one can only hope to attain results which are constant and reproducible under a given set of conditions. This will no doubt still be the case if Mr. Burrage's valuable suggestion of flushing out is adopted; it is, however, an addition to technique which should be generally introduced.

In the limits available in this discussion it is impossible to go into further detail here, but it is hoped that a review of existing methods with recommendations may be available shortly.

Professor H. S. Taylor (*Princeton*) (*communicated*): The alternative to activated adsorption suggested in the paper by Allmand and Chaplin and that by Burrage cannot possibly be applicable to the cases studied by Taylor, Williamson and Sickman dealing with MnO , $\text{MnO} \cdot \text{Cr}_2\text{O}_3$ and ZnO . For, in these cases, the conditions laid down by these authors for preparation of the surfaces were fulfilled by our experimental arrangements. We did not depend on evacuation alone for obtaining a clean surface. In each case, the oxide surfaces were "washed" for many

²¹ This vol., p. 191.

²² Langmuir, Becker (this Discussion).

hours with a stream of purified hydrogen gas at temperatures 100° higher than the highest temperatures at which adsorption experiments were subsequently made. Furthermore, the order of our adsorption measurements was such that it corresponds with the crucial experiment suggested by Allmand and Chaplin. Our isotherm on $\text{MnO} \cdot \text{Cr}_2\text{O}_3$ at -78° C. was measured after the higher temperature experiments, and specifically after the isotherms at 305 and 444° C. The experimental data show no adsorptions at -78° C. corresponding to both activated and unactivated adsorptions; on the contrary, an adsorption one order *lower* in magnitude than the data above 300° C. The same order of experiment held for the zinc oxide studies with, however, a smaller difference in magnitude between activated and unactivated adsorption. Similar conclusions follow from more recent unpublished work on oxides in Manchester and Princeton.

We cannot understand and would welcome a physical picture of the increment of adsorption to gas displacement of the order of 10^4 to 1 in cases studied by Allmand. Our only idea in this connection is that it may be a process analogous to that contained in the recent work of Frumkin (this Discussion) in that small amounts of platinum accelerate hydrogen adsorption by charcoal. But, in Frumkin's case, there is no such ratio as 10^4 : 1 for the amount adsorbed.

Professor A. F. Benton (*Virginia*): Professor Allmand and Dr. Burrage in their communications to the discussion suggest the possibility that the phenomena observed in activated adsorption are to be ascribed to a slow displacement of impurities from the surface. They claim that the displacement of a trace of impurity results in a relatively very large increase in adsorption. Whatever the facts may be in respect to adsorption of vapours at charcoal surfaces, Dr. Burrage errs in stating that Benton and White found that a small amount of carbon monoxide caused a very large drop in the quantity of hydrogen adsorbed by the finely divided metal. In the numerous cases studied we have never found a decrease in adsorption exceeding the amount of impurity present, and in many cases there has been an *increase* in adsorption. Professor Allmand proposes a crucial experiment. After removal of the offending impurities by repeated operation at higher temperatures, will a new experiment at lower temperatures where previously only unactivated adsorption occurred, check the earlier result or will the adsorption be much increased? In our work with metals we have repeatedly satisfied these conditions, and always with the result that the adsorption at the lower temperatures has remained unaffected. Throughout the work the first isotherms obtained, both at higher and at lower temperatures, were found to be closely duplicated by frequent subsequent check runs. To cite a particular example, two isotherms for hydrogen on copper at -183° (Runs 27 and 44) showed very satisfactory agreement, in spite of the fact that in the six months' interval between these runs the copper was in almost continuous use in studies of the *activated* adsorption of hydrogen at higher temperatures. It should be noted also that all our metals were prepared by reduction with hydrogen *in situ* for many days at temperatures higher than any employed in the adsorption studies. Under these conditions a displacement of "impurities" during the measurements of hydrogen adsorption would hardly be expected.

Professor Frumkin (*Moscow*) (*communicated*): In his paper entitled "Criticism of some Experimental Evidence for Activated Adsorption"

Burrage states: "Burstein and Frumkin evacuated their charcoal for twenty-seven hours at 200°, and obtained 'an oxygen-free charcoal surface.' In this laboratory charcoals have been evacuated at 800° for very much longer times, and yet have given off appreciable amounts of carbon monoxide continuously over a long period during the subsequent investigation of a vapour isothermal."

This critical remark is based on a misprint in the advance proof of the paper of Burstein and Frumkin. Actually the charcoal was outgassed of course not at 200°, but at 900°. Besides, before the outgassing the charcoal was heated for some time at the same temperature in a hydrogen atmosphere. From numerous investigations carried out in this laboratory it would appear that such a treatment is quite sufficient to ensure a practically complete removal of the oxygen from the charcoal surface.

Professor A. F. Benton (*Virginia*) said, in regard to the paper of Professor Bonhoeffer and Dr. Farkas: It may quite possibly be correct to assume that the rate at which hydrogen is adsorbed in the "atomic" form is equal to the observed rate of the *ortho-para* hydrogen conversion. Such an assumption is supported not only by the studies of Taylor and Sherman contributed to this Discussion but also by the recent work of Emmett and Harkness,²³ in which it was found that the rate of the interconversion at an iron surface first becomes measurable in the same temperature range in which activated adsorption makes its appearance. On the other hand, in treating the energy exchange between gaseous hydrogen and solid surfaces, the process of *physical* adsorption cannot be ignored. In fact the evidence now available indicates that this last process must be the principal factor in energy exchange, at least at the lower temperatures.

Professor E. K. Rideal (*Cambridge*) said there were two aspects of the process of activated adsorption which appeared to present certain peculiarities. In the first place it was clear that over a certain temperature range gas was taken up with measurable velocities. How was this brought about? Experiments conducted at Cambridge over a number of years had shown fairly conclusively that gases can travel over oxide and metallic surfaces and also penetrate into the fine structure of the metal with finite velocities and that these processes which doubtless involve the jumping from atom to atom are pseudo-chemical in character in that there is an energy of activation required or a potential hump to get over. The slow uptake of gas in the low temperature range of activated adsorption must be due either to the opening up of new centres of activation on the metal surface itself or due to the diffusion away of activated molecules (or atoms) from a few previously existing centres of activation. He (Rideal) held the latter view, in the light of the effect both of sintering and of poisons on the phenomenon. The second point which seemed curious was that in many cases of the phenomenon of chemi-adsorption, the compound formed existed as a film. In the case of a film of tungsten iodide about 10 molecules thick it still possessed a characteristic dissociation pressure. Would a unimolecular and insoluble film of a chemi-adsorbed compound possess any such unique properties? The rate of formation under such conditions would probably be autocatalytic in behaviour since these reactions in bulk are interphase reactions.

²³ *J. Am. Chem. Soc.*, 54, Jan., 1932.

Dr. Farkas (*Frankfurt*) said: In answer to Professor Rideal's question as to whether the discontinuities observed with nickel are due to melting or to increased mobility of the adsorbed hydrogen layer we suggest the following. Two independent methods (catalysis and heat exchange) show that hydrogen may be bound to nickel in two different ways. In one of these, in our "hydride," this bond is particularly strong, in the other it is comparatively weaker. Inasmuch as the decomposition of the hydride is not accompanied by evolution of gas, as proved by special experiments, we are inclined to believe that we are dealing with a melting or increased mobility of the adsorption layer. Between these two possibilities we see no difference. The observed decomposition curve does not correspond to a thermodynamical equilibrium, since there is a temperature fall in the gas phase as well as a temperature jump at the boundary of the metal and the gas. Thus it is not permissible to draw conclusions on the strength of the hydrogen-metal bond from this curve.

Professor Taylor (*Princeton*) (*communicated*): I cannot agree with Dr. Frankenburg that "it is remarkable and *at present inexplicable*" that increasing portions of the metallic surface are rendered accessible to activated adsorption of hydrogen and nitrogen on tungsten. A full comprehension of the concept of activated adsorption provides an adequate theoretical explanation for these cases as well as for the observation of Frankenburg and Hodler that "the fraction of a given surface capable of entering into chemical reaction . . . grows with increase of temperature." All the measurements thus far obtained of the activation energies of activated adsorption show that these are small for the first areas covered and show a progressive increase for increased covering, probably up to a maximum value. Thus, Taylor and Williamson found on $\text{MnO} \cdot \text{Cr}_2\text{O}_3$ surfaces that for the first 10 c.c. adsorbed the activation energy was $E = 5900$ cal. For the three succeeding amounts of 5 c.c. each the values were $E = 9500, 10,400$ and $10,400$ cal. respectively. It is obvious from this that at a temperature, T , at which the first 10 c.c. will be adsorbed with measurable speed the second area (10th-15th c.c.) will be covered at a rate $e^{-(9500-5900)/RT}$ of the rate for the first area covered. At a temperature $T = 300^\circ \text{K}$. this represents a rate $e^{-3600/630} = e^{-6}$ or 1/400th of the initial rate. It is obvious that such coverage would only be attained in impractically long intervals of time. The same is true to an even greater degree for the areas covered with still higher activation energies. Increase of temperature shortens the time required for such coverage, the rate increasing exponentially with the temperature. Similar conclusions result from the data of Taylor and Sickman²⁴ on zinc oxide surfaces. Velocity data on tungsten surfaces would undoubtedly reveal a similar state of affairs. The hydrogen data of Frankenburg and Hodler indicate activation energies for hydrogen adsorption on tungsten of the same order of magnitude as found by us on oxide surfaces and markedly higher than those obtaining with metals such as Ni, Pt, Pd and Cu. With nitrogen the activation energies are obviously greater since the rising section of the curve of isobars extends from 60 to 600° C.

It is of interest to record that from Frankenburg and Hodler's isobars for hydrogen at 0.1 mm. and 0.5 mm. (Fig. 5) approximately equal areas are covered at 200 and 300° C. respectively. A heat of

²⁴ *J. Am. Chem. Soc.*, **54**, 602, 1932.

adsorption of approximately 8600 calories per mol. is calculable from these data. It is evident that this does not represent a van der Waals' adsorption of hydrogen and is comparable in magnitude with the heats of activated adsorption (9000-15,000 calories) found on such metal surfaces as copper and nickel.

Dr. Frankenburger (*Ludwigshafen*) in reply wrote: There is no doubt that a sharp increase of the activation energy necessary for adsorption on the successive parts of the surface of the adsorbent which are brought into action explains the fact that within a stated temperature range the surface particles which "actively adsorb" with still measurable velocity decrease rapidly with fall of temperature. Further, it follows from a like inconstancy of the activation energy that: (1) at a given temperature the increase in the velocity of activated adsorption over a larger surface range cannot be represented by a reaction of the first order with a single velocity constant, but only by a reaction of the first order with continually decreasing constant; and that (2) the temperature coefficient of the adsorption velocity increases rapidly as the thickness of the coating increases. These criteria for the validity of Taylor's explanation are found in the cases he cites; we have not yet so exactly proved it for the active adsorption of H_2 and N_2 on tungsten as to be able to decide between the two explanations. The results on the kinetics of ammonia decomposition on tungsten cannot be explained according to Taylor's scheme, so far as our own analysis of the velocity of decomposition, either as a bimolecular or a monomolecular reaction, is correct. The above-mentioned criteria which are applicable to this scheme do not tally with this surface process. For instance: (1) the velocity, whether of the bimolecular or of the monomolecular part of the total at a given temperature, independently of the magnitude of the surface particles whether already blocked or in a fresh reactive condition, is represented by a single characteristic constant (Table II.); (2) the temperature coefficients of both processes are, on the whole, constant in relation to the surface taking part in the reaction; this leads us in the ordinary way to the conclusion that there is, also, a constancy of the activation energy of both decomposition processes over the whole of the surface particles. For this latter condition we maintain, as indeed for the increase of reacting materials with rise of temperature, that without further assumptions the effect is still incapable of explanation.

Professor H. S. Taylor (*Princeton*) said: Tables I. and II. of the paper of Maxted and Hassid illustrate the experimental difficulty of separating van der Waals' and activated adsorption of hydrogen in the case of such metals as platinum, nickel and copper. This arises from the low energies of activation of hydrogen on the metals in question so that activated adsorption is becoming rapid in regions of temperature where van der Waals' adsorption is also occurring. A separation into primary and secondary adsorption by extrapolation of the adsorption-time curves to zero time does not give van der Waals' adsorption only. It gives a summation of this latter and the activated adsorption that is occurring with low activation energy. Further, in all cases investigated by the present writer, extrapolation to zero time has been a very arbitrary process owing to the continuous nature of the curves even in the earliest time intervals. With the oxide surfaces studied this difficulty of separating van der Waals' from activated adsorption of hydrogen does not exist owing to a low van der Waals' adsorption and an activated adsorption which is slow even in the temperature range 0-100° C. It is

with these oxides that the cleanest-cut evidence of the two types of adsorption has been obtained. The data show that the heat of activated adsorption is one order higher than that of van der Waals' adsorption. As this is true also of the metals the determination of heats of adsorption from -190°C . upwards should provide the most marked differentiation of the two types of adsorption of hydrogen on metals. Carbon monoxide on oxides is similar to hydrogen on metals in that there is a marked overlap of van der Waals' and activated adsorption (unpublished data by Williamson in Princeton and Whitworth in Manchester) at certain temperatures.

The inability of Maxted and Hassid with the method of extrapolation to distinguish sharply between van der Waals' and activated adsorption detracts considerably from the value to be attached to their observations of the variation of "primary" and "secondary" adsorption with temperature. Were van der Waals' and activated adsorption separated they would each be found to decrease continuously with increase in temperature at a given pressure. Also, since their "primary" adsorption certainly includes some activated adsorption the influence of a poison is less surprising.

The observations of Maxted and Hassid relative to the increased hydrogen evolution with increased temperature of evacuation is the strongest possible experimental evidence that different areas of the surface have widely different activation energies of desorption and therefore of adsorption.²⁵

Dr. E. B. Maxted (*Bristol*), in reply, said that, in spite of the possibly greater difficulty in extrapolating to zero time with metals, compared with oxides, his collaborator and he had purposely employed metallic adsorbents in order to avoid the possibility of catalysed reduction which is present if oxides are used, the criterion for pure adsorption, unaccompanied by reduction, being an observation in every case that the hydrogen adsorbed on an oxide can be removed as such and not in the form of water. Even with metals, however, the mathematical differentiation between the almost instantaneous phase and the slow subsequent process was reasonably sharp, as would be seen on referring to Fig. 2.

The influence of a poison on the rate of adsorption would seem to confirm a continuous variation in surface energy—and therefore in activation energy—from point to point in the surface rather than the occurrence of, for instance, two types of adsorption, associated respectively with a high and with a relatively low energy of activation, the energy differences being inherent in the surface and not necessarily in differing adsorption types.

Professor H. S. Taylor (*Princeton*), with reference to the paper by Professor Garner, said: Does not the introduction of the case of "irreversible adsorption" of hydrogen and of carbon monoxide on zinc-chromium oxide surfaces which hold adsorbed oxygen really becloud the issue. In such cases are we not merely studying an interaction between adsorbed oxygen and adsorbed hydrogen (or carbon monoxide) on surfaces of zinc-chromium oxide. There is definite evidence in some American work that the oxygen is adsorbed on the surface even though the adsorption is, in some cases, accompanied by a change in colour of the oxide. The phenomenon is not peculiar to zinc-chromium oxide but is also found with chromium oxide in admixture with either manganous oxide or copper oxide.

²⁵ See Taylor, *Chem. Reviews*, Aug., 1931.

May it not be that the cases of real irreversible adsorption, such as oxygen on charcoal or tungsten, involve the sharing of electrons of oxygen and those of the adsorbent from the lower electron shells? In the case of zinc oxide, cited by Garner, the work in Princeton by Sickman shows no evidence of a reduction of zinc oxide to zinc as would be the case if Garner's mechanism were sound. It seems probable that any water formed resulted not from oxide reduction but from interaction with adsorbed oxygen.

With respect to the values for adsorption on the rising section of isobars showing minima and then maxima it is to be observed that these can in no way be treated as equilibrium values. The figures given really depend on the length of time allowed by the investigator before taking his final reading. It can readily be calculated from velocity data at higher temperatures and from the magnitude of the activation energy that in many cases times of the order of 10^8 years would be needed for equilibrium to be attained, precisely as in equilibrium measurements in chemical reactions. Such data on rising curves cannot therefore be used for estimating heats of adsorption. In our view, for a given surface area covered, there is a characteristic heat of van der Waals' adsorption and a characteristic heat of activated adsorption irrespective of the temperature at which the activated adsorption is secured, neglecting, of course, the second order variations in the heat quantity due to specific heat variations of factors and products.

Mr. M. G. Evans (*Manchester*) said: Professor Garner classes under what he calls irreversible adsorption such cases as the adsorption of oxygen on charcoal and tungsten where the oxides of charcoal and tungsten are removed on desorption. This appears to be a case of surface compound formation and not an adsorption process, although the compound formation may be a process subsequent to the adsorption. There seems to be a very definite distinction between adsorption in any of its forms and this case of surface compound formation, the latter being characterised by the fact that the "binding" between the oxygen atoms and the surface atoms of the solid is firmer than the "binding" between the surface atoms and the underlying atoms of the solid.

Dr. J. T. Randall (*London*) said: I notice that Mr. Kingman refers to driving off the adsorbed hydrogen at 950° C. Some very similar experiments have recently been carried out at Wembley under approximately the same conditions of pressure and temperature and no free hydrogen was given off by the charcoal. No change in pressure was produced when a palladium tube attached to the apparatus was heated externally. The product of desorption has not yet been identified beyond the fact that it is still gaseous at liquid air temperatures.

Dr. H. K. Cameron (*London*) said: In the absence of Professor Frumkin and Dr. Burstein it might be of interest to draw attention at this point to a statement in their paper. They say, "It is not quite certain whether hydrogen adsorption by charcoal is completely reversible, since on outgassing the charcoal which has adsorbed hydrogen the formation of small amounts of a dark deposit on the walls of the reaction vessel is always observed; this is probably due to the decomposition of some hydrocarbons." It would be interesting to know whether Mr. Kingman has ever observed this, or whether it agrees with the experience of Mr. Randall. It may be that we are here also concerned with an example of irreversible chemisorption.

Professor E. K. Rideal (*Cambridge*) said : Some of the experiments of Frumkin appear pertinent in the light of Mr. Kingman's work. Frumkin has examined the rate of uptake of hydrogen by charcoals containing small quantities of platinum. The rates are measurable and increase with increase in platinum content. This phenomenon is usually interpreted on the view that the platinum charcoal complexes serve as active spots, and hydrogen activated at these spots migrates into and over the charcoal surface in the activated state (according to some as atoms). Frumkin found that on immersion the charcoal as a whole acquired a characteristic potential; active spots were not identifiable electrometrically. It seems likely that, if the above interpretation is correct, the amount of current capable of being drawn from the charcoal, rather than the reversible potential, should characterise the number and nature of the active spots.

Professor W. E. Garner (*Bristol*), in reply, said : With regard to the irreversible adsorption of hydrogen which occurs on oxidised $\text{ZnO-Cr}_2\text{O}_3$ catalysts, Professor Taylor suggests that this is due to a reaction between adsorbed oxygen and hydrogen, which process is presumably followed by the irreversible adsorption of the water formed. In Kingman's experiments, 70 c.c. of hydrogen were adsorbed irreversibly by 10 gms. of catalyst. The change in colour which accompanies the reduction is an indication that the oxygen was chemically combined with the $\text{ZnO-Cr}_2\text{O}_3$ surface. It is possible that a higher oxide is formed and that this is reducible by hydrogen or carbon monoxide. Whether or not the oxygen is adsorbed or chemically combined can be settled by determination of the heat of adsorption of oxygen on the reduced catalyst. In any case, as a result of the reaction, the hydrogen is more firmly held on the surface than it is on a reduced surface. This shows there are at least three distinct types of adhesion of hydrogen to oxide surfaces.

Equilibrium is not attained on any part of the adsorption isobars on metals and oxides within a reasonable time. The work of Maxted and Hassid on the adsorption of hydrogen by nickel, however, shows that the adsorption is as complete on the rising section of the isobar as on the subsequent falling section. The question at issue, the temperature coefficient of the heat of adsorption, can be settled by experimental measurements.

Dr. Kingman analysed the hydrogen desorbed from charcoal at 950° and found it contained negligible quantities of hydrocarbons.

In reply to Mr. Evans, irreversible binding of atoms on solid surfaces in the past has been referred to as chemi-sorption. This form of adsorption is undoubtedly due to a chemical combination between the gas and the atoms on the surface of the solid. In the broad sense of the term, "activated" adsorption is also a form of chemical combination with the surface atoms, although in this case the adsorbed atoms possess greater mobility along the surface than is the case when they are irreversibly adsorbed. In order to distinguish between the two types, I have called them respectively irreversible and reversible activated adsorption.

Dr. C. Schuster (*Ludwigshafen*) said, with regard to the paper of Professor Taylor and Dr. Sherman :—

(1) It would be interesting to ascertain whether the active charcoal used by Taylor and Sherman has the power of inducing hydrogenation of adsorbed hydrocarbons and, on the other hand, whether the active

charcoal which we have utilised in our hydrogenation experiments is suitable for catalysing the hydrogen transformation.

(2) Negative temperature coefficients such as Professor Taylor has mentioned appear to be a common phenomenon in the case of hydrogenation reactions. In the hydrogenation of adsorbed ethylene, propylene and the various butylenes on the most different hydrogenation contact materials, we have established the presence of such maxima with corresponding decrease of reaction velocity on increase of temperature. For different contact substances and different hydrocarbons the maxima are at somewhat different temperatures; they do not depend upon the hydrocarbon adsorption, but manifestly only upon the hydrogen and its adsorption.

Dr. E. Cremer and Professor M. Polanyi (*Berlin*) communicated: Some experiments done recently with *solid hydrogen* have shown, that the transformation *ortho* \rightarrow *para* goes on in this state of hydrogen just as well as in the liquid state. This proves the existence of a homogeneous *ortho-para*-reaction at about 12° abs. and makes it extremely probable, that the transformation observed in the liquid state by Bonhoeffer and Harteck represents also the same homogeneous reaction. Both the absolute value of reaction velocity (half-period of about 40 hours) at the very low temperature of 12°, as well as the fact of its proceeding here just as quickly as at the boiling-point of hydrogen (20° T.) prove, that it is not accompanied by any activation energy.

On the other hand it can easily be shown, that the process cannot be due to a quantum mechanical effect in the sense of Born and Frank's ideas of adsorption catalysis: because if it were, its velocity would be much greater in the denser solid state, than in the less dense liquid one.

It follows, that the *ortho-para*-transformation can be caused merely by the van der Waals' forces present in solid hydrogen. It is here certainly not a chemical reaction in the sense of an atomic exchange. We feel, therefore, doubtful whether the *ortho-para*-transformation in adsorbed layers should generally be thought of as a chemical reaction. Especially the transformation caused by catalysts at very low temperatures could be perhaps only a more accentuated form of the process going on in the liquid and solid phase; a greater velocity being caused by the stronger cohesive forces, which act in the field of adsorption.

Dr. A. Farkas (*Frankfurt*) said: Professor Taylor is of the opinion that the *ortho-para*-hydrogen-conversion on charcoal at low temperatures is due to activated adsorption. We can conclude of temperature independence of this reaction observed by Rummel that this energy of activation must be less than 200 cal. Therefore I wish to ask Professor Taylor whether we could call this hydrogen adsorption an activated adsorption, since we have experimental evidence (Kingman) that there is at high temperatures a hydrogen adsorption on charcoal with the energy of activation of 30,000 cal. We would rather suggest that the mechanism of the *ortho-para*-hydrogen-conversion at low temperatures on charcoal is very different from the mechanism on metals for example, at high temperatures and this reaction needs neither activated adsorption nor activation energy, but is perhaps similar to the *ortho-para*-hydrogen-conversion observed in liquid (Bonhoeffer and Harteck) and in solid (Cremer and Polanyi) hydrogen.

Professor H. S. Taylor (*Princeton*), in reply, said: In view of the communication of Dr. Cremer and Professor Polanyi, the conclusions of Taylor and Sherman might be amended to read that the *rapid*

conversion of *ortho-para*-hydrogen at surfaces is to be associated with the activated adsorption of hydrogen. The half-life period of forty hours involved in the conversions of solid and liquid para-hydrogen are entirely without significance in all the surface reactions studied by us in which activated adsorption is involved.

The activated adsorption of hydrogen which we believe to be involved in *ortho-para*-hydrogen at charcoal surfaces is not that involved in the experiments of Kingman at high temperatures which has an activation energy of 30,000 cal. Rather is it such activation as occurs at very low temperatures, as low as the boiling-point of hydrogen, and involving, as the completed calculations of Sherman and Eyring now show, activation energies of less than 5000 calories for favourable C-C distances, e.g., 3.5 Å.

We do not believe that there is any fundamental distinction between the conversion at carbon and at metal surfaces. Our experiments on copper (on which, contrary to Bonhoeffer and Farkas, we found marked activity even as low as 85° K.) are parallel to the charcoal experiments in so far as they reveal a falling-off in the conversion rate in the temperature range in which activated adsorption of hydrogen is rapidly decreasing. This points to a bimolecular interaction on copper in a higher temperature range similar to that we found from -78° to 0° C. on carbon.

Mr. B. Lambert (*Oxford*) said: There are certain aspects of adsorption which have hitherto attracted little attention but which *may* afford important clues to the fuller understanding of this very complex subject.

The increasing use of the term "van der Waals' adsorption" seems to imply an assumption that the behaviour of gaseous molecules towards an absorbent solid is more or less defined (or circumscribed) by the critical constants of the gases. Very little account seems to be taken of possible effects due (a) to differences in the sizes of the gaseous molecules, or (b) to any other peculiarities of the gaseous molecules not associated with the critical constants. There is already evidence to show that these considerations cannot be neglected, and it is possible that they may be very important.

(a) *The Size of the Gaseous Molecule*.—Recent work, carried out in Oxford by the writer and his collaborators, on the adsorption of condensable vapours by silica gel and two types of ferric oxide gel, has established beyond any doubt that hysteresis phenomena are associated with real equilibrium conditions in benzene-ferric oxide gel and ethyl alcohol-ferric oxide gel systems; but, in the analogous benzene-silica gel and ethyl alcohol-silica gel systems there is complete absence of hysteresis phenomena. In the case of the water-silica gel system there is, however, definite evidence of hysteresis. An examination of the comparative pressure-concentration isothermals of all these systems shows that the adsorptive processes (for benzene and for ethyl alcohol) of the two analogous dehydrated gels are essentially different. The molecules of benzene and alcohol are approximately equal in diameter, and so the striking differences between the pressure-concentration isothermals are probably due to differences in the internal structures of the two gels.

Neither layer theories of adsorption, nor theories involving the conception of condensation within fine capillaries, can, of themselves, afford a satisfactory explanation of the results, unless consideration be given to the relation between the diameters of the vapour molecules and the

diameters of the capillaries. In this connection, it is interesting to consider the striking differences between the comparative pressure-concentration isothermals for silica gel-vapour systems when the vapours are water, benzene, alcohol. The shape of the isothermal for the water-silica gel system is markedly different from those of the benzene-silica gel and alcohol-silica gel systems and, since we are dealing with the same solid adsorbent, this difference must be due to some peculiarity in the water vapour molecule; we know that the water-vapour molecule has a diameter much smaller than that of the benzene or alcohol, but it is not yet possible to say whether this is the main cause of the peculiarities of the system.

(b) "*Selectivity*" in Adsorption.—We have very little quantitative knowledge of adsorption under conditions when two gases are competing for a solid adsorbent surface and it is, at present, impossible to say, with any certainty, how the adsorption of a particular gas by a given adsorbent solid is affected by the introduction of another gas into the adsorption system.

Hückel has published a theoretical consideration of the problem, but he takes no account of the possibility of *selective* adsorption, and his conclusions are based only on the simple physical properties of the gases when considered separately.

Isolated cases are known in which a solid adsorbent shows marked selective (or the reverse) adsorption, but information on the matter is meagre and qualitative. Accurate results on adsorption from gas mixtures are required in order that we may judge whether or not this selectivity is a common phenomenon in adsorption.

The importance of a knowledge of adsorption from mixed gases is obviously of the greatest importance in catalysis; but, if accurate data, in sufficient quantity, were available, it must also lead to a clearer understanding of the attractive forces between solids and gases.

PART III.—THEORIES OF ADSORPTION.

Dr. A. Farkas (*Frankfurt*) said with regard to Professor Lennard-Jones' paper: From experiments on volatility¹ and from spectroscopic data we know that the heat of dissociation of the hydrides of Cu, Ag and Au is about 50,000-70,000 cal. It is possible that an activated adsorption results in the formation of such hydrides on these metals, and that it is easier to evaporate the whole hydride molecule than to evaporate the hydrogen only. Thus we could explain our results which show Cu, Ag and Au-wires to be inactive in the *ortho-para*-hydrogen-conversion.

Dr. K. G. Emeléus (*Belfast*) said: Would it not be possible to obtain information about the binding forces in adsorption from a study of the temperature variation of the specific heat of a solid (a) with a clean surface, and (b) when the surface has adsorbed heavily? Would the magnitude of such an effect bring it within the scope of practical investigation?

Mr. N. J. Hassid (*Bristol*) said: In order to explain results recently obtained with H₂ on Cu (Benton), and H₂ on Ni (Maxted and Hassid), it is necessary to assign to those molecules undergoing activated adsorption, a wide range of activation energies.

¹ A. Farkas, *Z. physik. Chem.*, **5B**, 467, 1929.

Dr. F. J. Wilkins (London) (communicated): (a) *The adsorption of argon on potassium chloride.*—I am very much interested in the recalculation of the heat of adsorption of argon on potassium chloride. From measurements made at liquid air temperatures I have found that the amounts adsorbed must be at least ten times smaller than those expected if the heat of adsorption were between 2000-2500 cal. The recalculated figure of about a half this gives an adsorption of just about the right order.

(b) *The heat of activation of the intergranular solution process.*—The heat of activation for diffusion along the outer surface need not necessarily be the same as the heat of activation for diffusion through a crack owing to the overlapping of the potential fields due to the two sides of the crack. This, in the case of very narrow cracks ought surely to modify the nature of the field inside the crack considerably. Some work on the reduction of superficially-oxidised copper is of interest from this point of view.² In this work it was shown that the rate of diffusion along the oxide/hydrogen interface to a crack (or, evaporation from the interface into the oxide film) is very much slower than the rate of diffusion through the crack. Is it possible that there can be an "interference" of the fields of the atoms lying on each side of the crack so as to produce something like a plane of constant potential energy? If this were true, once atoms had been activated sufficiently to reach this potential plane they would enter the crack and proceed down it without hindrance provided the time taken to traverse the crack is much smaller than the mean life of the diffusing molecule in the activated state. The thickness of the oxide film, *i.e.*, the length of the crack, was never greater than 10^{-4} cm.

The diffusion of oxygen through films of the same type is quite different.³ Here the rate of diffusion through the oxide film is slow. The heat of activation was interpreted to be the energy which a diffusing oxygen molecule and two associated vibrators on opposite sides of a crack must have in order that the vibrators could separate far enough apart to permit the oxygen to diffuse. It is not impossible that this type of diffusion is the one which applies when hydrogen dissolves in copper. If this is true, the heat of activation determined by Ward is not physically the same thing as the heat of activation calculated by Professor Lennard-Jones.

Dr. L. Tronstad (Trondheim, p.t. Cambridge): During this discussion we have learned that the adsorption of gases by a solid must be considered as a very complicated reaction indeed. One has for example to deal at least with (1) an ordinary adsorption and probably also (2) an "activated" adsorption of the gas atoms or molecules at the free surface, further (3) a diffusion of adsorbed gas from the surface into the fissures or "Smekal cracks" (this process may also be an activated one), as well as (4) a diffusion of superficial gas into the crystal lattice, both from the free surface and the cracks, with the resultant formation of a solid solution or a solid compound. If all these reactions take place *simultaneously*, as in fact usually will be the case at higher temperatures, it seems very difficult to draw conclusions about the question of the mechanism of the adsorption from experimental determinations of the *total amount* of adsorbed gas.

² Wilkins, *J.C.S.*, 330, 1931.

³ Wilkins and Rideal, *Roy. Soc. Proc.*, 128A, 394, 1930; Wilkins, *ibid.* p. 407.

It is therefore important to employ more *definite* experimental conditions, under which the amount of gas taken up will only be due to a certain number (if possible only to a single one) of the reactions mentioned, or under which certain possible reactions have already been studied quantitatively in detail. For example, by investigating the ordinary and the "activated" superficial adsorption, the experimental conditions should be chosen in a way, so that the rate of diffusion into the lattice would be either known or extremely low, and that the rate of diffusion into the cracks would be as low as possible. The solubility is usually low at lower temperatures, and may therefore be neglected in comparison with the adsorbed quantity of gas, as mentioned during the discussion. At higher temperatures, however, where the "activated" adsorption should be more liable to take place, this solution cannot be neglected, unless the solid used in fact is proved to have a low solubility for the gas in question (for example nickel or cobalt and nitrogen). With respect to the diffusion into the cracks, experiments have shown that "Smekal cracks" and other crystal defects can no longer be detected by usual methods after suitable heat treatment.⁴ This fact indicates also the possibility of reducing the rate of diffusion into the cracks to a minimum, by employing heat treated single crystals of suitable size as the adsorbing solid.

As an objection to this method one might say, that the amount of adsorbed gas will be very small, as already mentioned by Professor Taylor during the discussion. Nevertheless, it is the quantity of adsorbed gas under such definite conditions, which is of the greatest interest, for example in the question of the "activated" superficial adsorption. Therefore, emphasis should be laid on the determination of adsorbed gas under these conditions.

The *optical method* introduced by P. Drude and mentioned by Professor Rideal in his introductory paper might also prove to be useful in this respect, both for investigating the physical state of the surface before adsorption (see the remarks of Dr. Hinshelwood and Dr. Roberts) and for determination of the amount of adsorbed gas. However, in this case only plane reflecting surfaces are to be employed (polished glass, metal mirrors, mica and other crystals with good cleavage).

Dr. E. Hückel (Stuttgart) said with reference to Professor Lennard-Jones' paper: It seems to me very important to make systematic experimental investigations on the adsorption of the inert gases on pure charcoal to get full information on the influence of the so-called "dispersion forces" on the adsorption, as well as on the equation of state of the adsorbed layer, since in this case it is to be expected that only these dispersion forces are present.

Mr. M. G. Evans (Manchester) said: It would be of interest in connection with Fig. 3 and the discussion relevant of Professor Lennard-Jones' paper to know if the case of complete dissociation discussed is an extreme case and whether other curves of the form of curve 2 are possible indicating various stages of distortion of the adsorbed molecule of which complete dissociation is the limit.

Mr. A. R. Ubbelohde (Oxford) said: The picture of activated adsorption given in § 3 throws light on the effect of adsorption of gases on the high frequency resistance of metals, observed by H. Dobretsberger.⁵

⁴ See for example A. Smekal, *Physikal. Z.*, **32**, 187, 581, 1931.

⁵ *Physik*, **65**, 334, 1930.

Presumably the effect for van der Waals' adsorption would be much smaller.

Professor A. F. Benton (*Virginia*) said: In connection with the discussion of the forces involved in physical, or van der Waals' adsorption, I wish to call attention to the fact that the heats of *physical* adsorption of a given gas on a series of different surfaces are in large measure independent of the nature of the surfaces. This conclusion will be apparent if one examines the numerous cases cited by Kruyt and Modderman,⁶ which, together with more recent data, cover the heats of physical adsorption of a number of gases at surfaces of charcoal, silica, metals, etc. It follows that the binding force exerted by the solid in physical adsorption is essentially non-specific. The heat of physical adsorption is in general only two to three times as great as the latent heat of vaporisation of the gas. This fact indicates that the lateral forces between neighbouring adsorbed molecules cannot be neglected in comparison with the forces between the physically adsorbed molecules and the adsorbent.

Mr. M. G. Evans (*Manchester*) said: The possibility of a molecule first being held to the surface by the van der Waals' force and then changing over to a firmer type of "binding" to the surface, as described by Lennard-Jones on page , seems to be realised in certain cases examined by Bangham.⁷ Bangham found that the instantaneous expansion of charcoal, caused by the sorption of pyridine, "slowly decreases on standing." If we assume that the major expansion of a solid such as charcoal is caused, as Bangham suggests, by the two-dimensional pressure exerted by the mobile molecules, then a firmer association of such molecules to the surface would reduce the expansion merely by reducing the mobility of the adsorbed molecules. In the case discussed by Bangham the slow decrease of the instantaneous expansion may be governed by the probability of molecules held by the van der Waals' force, attaining such energy that they may pass over the potential peak (Fig. 3) and become more closely held to the surface.

Dr. Cecil H. Desch (*Teddington*) (*communicated*): Professor Taylor remarks⁸ that the movement of molecules in two dimensions on a surface may be limited to the case where the attraction is only due to Van der Waals' forces, and that polar linking may completely suppress such movements. On the other hand, the experiments of Volmer clearly show that such movements may take place when the linking is a metallic one, as in the case of a growing crystal of zinc or cadmium. This type of non-polar linking is of great importance.

In discussing the mobility of molecules on the surface, account should be taken of the conditions introduced by a possible secondary lattice, the existence of which has now been made very probable. If, as seems likely, the spacing of the atoms in the lattice varies in a periodic manner, then the attraction as a molecule passes over the surface will change from time to time, and this fact may account for the very unsatisfactory quantitative agreement obtained in the calculations by the Russian authors. In fact, this secondary lattice may be found to play an extremely important part in determining the whole phenomena of adsorption on crystal surfaces.

Professor J. E. Lennard-Jones, in reply, said: It is difficult to say without a detailed calculation whether the activated adsorption of

⁶ *Int. Crit. Tables*, and *Chem. Revs.*, 1930.

⁷ *J.C.S.*, 1931.

⁸ This vol., p. 135.

hydrogen on copper results in the attachment of a hydrogen atom to one copper atom in the surface, analogous to a diatomic CuH molecule, or whether the hydrogen is shared equally by two or four neighbours in the same way that the valencies of the atoms in a metal are shared by many neighbours. But the fact that the heat of dissociation of the copper hydride molecule from its ground state is about 70,000 cal. supports the picture which I have drawn in § 3 and suggests that hydrogen is adsorbed in the atomic form as postulated in Fig. 3.

In reply to Dr. Emeléus: the specific heat of a solid would not be changed very much by an adsorbed layer, because the amount of gas adsorbed by about 100 grms. of metal is only of the order of 10^{-3} to 10^{-4} grms.

In reply to Mr. Hassid: there would, of course, be different activation energies for the different faces of a crystal. It may be that the value deduced from Ward's results is only a mean value, but there is no indication of this in the experimental results. The slow sorption seems to obey an exponential law quite accurately and the curve of $\log s^2/q^2t$ against $1/T$ gives only *one* slope. In this connection it is to be noticed that Ward found a heat of adsorption which was independent of the amount adsorbed.

If the interpretation of the activation energy suggested in my paper is the right one, there must be another and higher energy necessary for penetration of the lattice. At sufficiently high temperatures this higher activation energy must show itself and cause a change of slope in the $\log s^2/q^2t$ against $1/T$ curve. When this occurs it will indicate that real solution is beginning.

In reply to Dr. Wilkins: there will be an overlapping of the potential fields in *very narrow* cracks, but the forces which I postulate between an atom like hydrogen and a metal like copper are short-range forces and probably fall off very rapidly between (say) 1.5 Å and 3.0 Å. If the crack were so narrow that vibrators on opposite sides of a crack had to separate to allow an atom to diffuse, there would be little distinction between that case and the process of solution into the body of the metal. The energy of activation would be definitely higher than that for surface migration and diffusion down such narrow cracks would only occur at high temperatures.

In connection with the point raised by Mr. Evans, the curves in Fig. 3 are intended only to refer to two extreme cases. The lower curve (marked 1) applies to an approaching molecule AB which has the lowest possible vibration energy, the upper one to a molecule AB which has such large vibrational energy that it has dissociated. For molecules with intermediate amounts of vibrational energy, there will be intermediate curves.

I am glad to have Professor Benton's confirmation of the fact that the heats of physical adsorption depend mainly on the nature of atoms adsorbed and not on the surface, for this result follows theoretically from the discussion given in § 2 of my paper. I expect, however, that the heats of physical adsorption on non-metallic surfaces such as NaCl , etc., will depend on the nature of the surface.

Dr. N. K. Adam (*London*) (*communicated*), referring to the papers of Professor Magnus and Mr. M. G. Evans said: The attempt to describe the adsorbed layers on solid surfaces by a van der Waals' equation, or by any type of two-dimensional isotherm which suggests that their behaviour resembles that of a two-dimensional gas, seems to me very misleading.

Although these adsorbed layers are sometimes mobile, yet the mobility of adsorbed molecules along the surface is often incomparably slower than that of gas molecules in free space.

Professor Lennard-Jones has shown us that the molecules move along the surface in a series of very infrequent jumps, being firmly fixed to the surface nearly all the time. Surely it is improper to compare such a spasmodic and intermittent motion, even formally, to the behaviour of a gas.

Dr. Hückel (*Stuttgart*) said, with reference to Professor Magnus' paper:

The formula (3),

$$A = \frac{k_1 k_2 p - k_3 A^2}{1 + k_1 p - k_3 / k_2 A^2}, \quad (3)$$

which has been derived by Professor Magnus from a van der Waals' equation

$$(\pi - \alpha / \Omega^2)(\Omega - \beta) = RT \quad (2)$$

of the adsorbed layer is not correct. The exact thermodynamic treatment⁹ of the adsorption equilibrium, if that formula (2) holds, leads to an adsorption-isotherm not of the form (3) but of the form:

$$p = \frac{RT A e^{\left[\frac{\beta a}{1 - \beta a} + \frac{2\alpha}{R a} \right]}}{(1 - \beta a) K(T)}, \quad (a = A/O),$$

where $K(T)$ is some function of T which cannot be determined from the equation of state of the adsorbed layer. Therefore it seems to me necessary to revise the results on α and β derived by Professor Magnus from his equation (3).

Professor R. H. Fowler said: Professor Magnus has commented on the disagreement that has been found between the (relative) van der Waals' attractions of gas molecules (derived presumably from the a of van der Waals' equation of state) and the (relative) firmness with which the same molecules are attracted to a surface as shown by the heat of adsorption. I think he has advanced this disagreement as a difficulty for the theory that in many cases of adsorption gas atoms are held to the metal or other solid by forces of exactly the same origin as the van der Waals' attraction in a gas. I do not think it should be necessarily so regarded; Professor Magnus makes the important point that for molecules with a permanent dipole moment the forces binding them in adsorption to the solid may arise principally from their *orientated* dipole, while the dipoles they carry, owing to their *random* orientations in a gas, contribute in only a minor degree to the van der Waals' attraction. This is undoubtedly correct. But for molecules without a permanent dipole there is a second order polarisation effect which attracts them to each other in a gas or equally to a solid surface. The forces are identical in nature but need *not* be closely correlated in size, since we have to do in one case with the mutual polarisation of a pair of gas molecules and on the other with *one* of these molecules and another system altogether.

I would like, too, to utter a warning against the too literal interpretation of van der Waals' a and b as effects of molecular attractions and sizes respectively. When one comes to analyse carefully the equation of

⁹ The method is the same as in E. Hückel, *Adsorption u. Kapillarkondensation*, Leipzig, 1928.

state of a gas, one finds that there is only one way in which one can securely correlate the observations of the equation of state with intermolecular forces, and that is by comparing the observed second virial coefficient of Kamerlingh Onnes (roughly the first *small* deviations from the perfect gas laws) with a theoretical value computed from an assumed law of intermolecular force. No accurate use can be made of critical point data for this purpose. But one finds further that the so-called *a* and *b* terms of van der Waals' equation cannot be referred to distinct parts of the field of force; both attractive and repulsive regions contribute to *a* and both to *b* unless a quite arbitrary division is made of the second virial coefficient as to what part of it corresponds to van der Waals' *a* and what to his *b*, and unfortunately it is only for the combination of *a* and *b* that occur in the second virial coefficient that significant comparison with experiment can be made. Similarly, unless the equation of state of the adsorbed layer is analysed in the same sort of way, it is impossible to derive reliable values of the intermolecular forces between adsorbed gas atoms to compare with the similar forces between the same atoms when free. I imagine this could be done, but I doubt if it has ever yet been done except quite qualitatively. I do not, however, think that we have any reason for surprise if we find these forces between adsorbed molecules different from those between the same molecules when free. There is, of course, the effect of orientation to which Professor Magnus has referred, which can be of great importance. And even apart from this, it seems to me that a qualitative agreement is all that we have reason to expect, except perhaps for the simplest adsorbed molecules, such as inert gas molecules.

Mr. A. R. Ubbelohde (*Oxford*) said, with regard to the paper by Professor Magnus: If the neighbouring molecules of an adsorbed substance repel one another strongly, the presence of a second type of molecule acting as a dielectric may weaken these forces and thus increase the adsorption of the first type.

Professor A. Magnus (*Frankfurt*) (*communicated*): I fully agree with Professor Fowler that the constants *a* and *b* of the van der Waals' equation cannot be used literally in their respective original sense. But, using the two-dimensional equation for adsorbed gases without a permanent dipole, the fact of the negative sign of *a* as well as of *b* (experimentally found from adsorption measurements with CO_2 , C_2H_2 , C_2H_4), seems to me to prove that forces acting between adsorbed molecules can only be of repulsive character. The decrease of the heat of adsorption with rising pressure leads to the same conclusion, because the amount of the decrease in question equals the caloric effect of a two-dimensional Joule-Thomson effect producing a liberation of heat energy, which appears at the expansion of a gas, even at low pressures when the amount of surface occupation is so small that molecular volumes can be neglected. These two facts seem to indicate the correctness of the opinion that the above-mentioned gases while being adsorbed are due to suffer deformations to dipoles which in parallel orientation show repulsive forces towards each other.

Dr. F. J. Wilkins (*London*) (*communicated*): The results of Dr. J. K. Roberts on the effect of impurities on the accommodation coefficient are similar in type to those which I have deduced recently from some work on intensive drying. Michalek and Rodebush¹⁰ have shown that while intensive drying leaves unchanged the vapour pressure of ammonium

chloride, it decreases the rate of vaporisation. Therefore, if P is the vapour pressure and V the rate of vaporisation we have,

$$V = k\alpha P,$$

where k is a constant and α is the accommodation coefficient. Since k and P are unaltered by intensive drying the decrease in V must be accompanied by a decrease in α , *i.e.*, the removal of impurities from the surface of ammonium chloride by intensive drying causes a decrease in its accommodation coefficient for molecules of its own vapour. Similar conclusions can be drawn from the work of J. W. Smith¹¹ on the decrease in the rate of distillation of ethyl bromide which accompanies intensive drying. A more detailed account of this work together with a theoretical discussion is to be published shortly.

Professor H. S. Taylor (*Princeton*) (*communicated*): The thesis of Dr. Ward's paper is that, because he claims to have established a slow activated diffusion, there is no necessity for activated adsorption. His thesis can very easily be disposed of by various considerations. In the first place, it is worth emphasising that to label the slow process observed by Ward as solution ignores the fact that the quantities of gas involved are one or two orders greater than the well-determined solubility data of the gas in question. This is evident from Table I. appended which shows adsorption and solubility data for hydrogen in copper and nickel and for oxygen in silver. These data also show how unjustified Steacie¹² is in claiming that solution will explain the activated adsorption data, a claim which Ward, apparently without any attempt at verification, has repeated.

In the second place, what Ward terms adsorption is "activated adsorption," and he himself has proved it. For he has measured the heat of adsorption showing it to have values in the neighbourhood of 10,000 cal. per mol. That such a heat effect is not to be associated with van der Waals' adsorption is evident from Benton's data (this Discussion). The van der Waals' adsorption, as shown by Benton, involves a heat of adsorption of about 1000 cal., and is entirely negligible in amount at room temperatures and upwards.

In the third place, Ward ascribes to adsorption what takes place *rapidly* at room temperatures. He ignores the fact that such adsorption would take place at slow and measurable rates at temperatures of -- 78° C. and lower.

Fourthly, the concordance found by Ward between his theoretical equation for the rate of *diffusion* and his experimental results does not constitute a sufficient proof that the process whose rate is measured is one of diffusion. Sickmann¹³ derived a formally identical equation on the basis that the slow process was one of activated adsorption, and obtained equally good agreement with experimental results.

Fifthly, the utmost that Ward can conclude from his work is that an activated diffusion *may* be superposed on an *activated* adsorption of hydrogen on copper. At present, no one can say, even if this be true, where the activated adsorption ends and the diffusion process starts, since it is quite possible that the process measured by Ward is, in part or wholly, activated adsorption of hydrogen on copper of which the activation energy is about 14,000 cal.

¹¹ *J.C.S.*, 2573, 1931.

¹² *J. Physical Chem.*, 1931.

¹³ *Thesis*, Princeton, 1931, *J. Amer. Chem. Soc.*, 1932.

Finally, it should be noted that there are many experimental cases of activated adsorption which are fundamentally distinguishable from the actual experimental conditions prevailing with copper in the range of temperature used by Ward. Thus, with zinc and molybdenum oxide mixture there is no measurable adsorption of hydrogen between -78°C . and temperatures over 100°C . The slow process occurs from 184°C . upwards with no initial rapid adsorption. Were the slow process one of diffusion it would not conform to Ward's thesis, that its amount was proportional to the extent adsorbed on the surface, since this is negligibly small in the range stated, and must be less in the higher temperature range.

The experimental and theoretical data presented in the present discussion establish unequivocally the existence of activated adsorption. They indicate the possibility, but do not conclusively establish the existence of activated diffusion.

TABLE I.—ADSORPTION AND SOLUBILITY DATA.

The following data show the best values for adsorption and solution of various gases in nickel, copper and silver, in c.c. per 100 grams.

(a) *Hydrogen and Nickel, $p = 760\text{ mm}$.*

$T^{\circ}\text{C} =$	-195	-183	-80	0	25	110	184	218	305	419	520	720
Ads. *	17.4	16.4	35.9	33.7		26.2						
Ads. †					58.5		52.8	47.2	36			
Sol. ‡							1.8	2.4	3.36	4.37	6.94	

* Benton and White, *J. Amer. Chem. Soc.*, **52**, 2325, 1930.

† Gauger and Taylor, *ibid.*, **45**, 920, 1923; supporting the nickel increases these figures 10-fold.

‡ Sieverts.

(b) *Hydrogen and Copper, $p = 760\text{ mm}$.*

$T^{\circ}\text{C} =$	-191	-183	-80	0	110	218	400	514	620	724
Ads. *	9.7	8.5	18.7	19						
Ads. †				15.5	13.9	9.3				
Sol. ‡							0.067	0.18	0.36	0.54

* Benton and White, *loc. cit.*

† Dew and Taylor, *J. Physic. Chem.*, **31**, 277, 1927.

‡ Sieverts.

(c) *Oxygen and Silver, $p \sim 760$.*

$T^{\circ}\text{C}.$	110°	200	300	400	500	600
Ads. *	30.7					
Sol. †		1.49	1.02	0.83	0.90	1.26

* Benton and Elgin, *J. Amer. Chem. Soc.*, **48**, 3027, 1926.

† Steacie and Johnson, *Proc. Roy. Soc.*, **117A**, 662, 1928.

Dr. A. F. H. Ward (Manchester) (*communicated*): Professor H. S. Taylor has suggested that because the extrapolated data of Sieverts for the solution of hydrogen in copper are of a smaller order than the amounts taken up slowly in sorption experiments at lower temperatures, the latter cannot therefore be attributed to diffusion into the solid. In my paper I discuss how the hydrogen is situated inside the metal and conclude that it is concentrated at the grain boundaries down which it has diffused. I made it clear that I did not consider it in solution uniformly throughout the lattice, but "persorbed," to use the word suggested by McBain in this discussion. One would therefore expect the

amounts of solution found by Sieverts to be smaller at higher temperatures where, on account of annealing, the Smekal cracks and their approaches to the surface would be decreased or destroyed. I have considered this point further earlier in the discussion.

In the second place, the part of the hydrogen adsorbed instantaneously had a high measured heat of adsorption (10,000-30,000 cals., depending on the degree of activation of the copper), but since it was complete within a few seconds the activation energy of the process must be very low—certainly much lower than the 14,000 cals. calculated from the temperature coefficient of the activated diffusion. As I point out in my paper, an activation energy can be calculated for any adsorption which takes place with a finite speed, so that for the rapid initial part of sorption the terms "adsorption" and "activated adsorption" are synonymous.

The case of the zinc and molybdenum oxide mixture mentioned by Taylor finally can be explained completely as due to adsorption plus diffusion. At low temperatures the true adsorption is measurable and decreases normally with temperature so that it cannot be experimentally detected above -78° . At 184° it may be assumed that the diffusion into the solid becomes sufficiently rapid to detect, for the diffusion coefficient increases exponentially with temperature for an activated diffusion process. It is fallacious to suggest that at this temperature the rate of diffusion into the solid cannot be proportional to the amount of gas adsorbed on the surface, merely because this is small, *and to give this as a reason that diffusion cannot occur*. Although a smaller adsorption on the surface would, at constant temperature, mean a correspondingly smaller rate of diffusion, yet on raising the temperature the diffusion coefficient increases much more rapidly than the adsorption decreases so that diffusion would still occur and would increase with rising temperature. If the adsorption were too small to detect experimentally, naturally no initial rapid adsorption would be found in this case to precede the diffusion.

Professor M. Polanyi (*Berlin*), referring to the paper of Dr. Schuster (*communicated*): The paper of Born and Weisskopf¹⁴ shows that chemical reactions can only then be caused by the "tunnel-effect" if the distance the atoms have to traverse from the initial state to the final state is very small. From the estimate given there, one can scarcely imagine that a distance larger than 1.5 Å.U. could ever be overcome in this manner.

However, no normal distance between the atoms of two different molecules has ever been found to be smaller, than, say, 3 Å.U., and if by any means the atoms of two molecules could be brought together to a distance of 1.5 Å.U., there would be no further resistance for the reaction to overcome.

I can only perceive a chemical field in which this effect could be active in transformations taking place in the inside of the molecule, where distances of the right order of magnitude could be realised, *e.g.*, for tautomeric changes.

Professor H. S. Taylor (*Princeton*) said: The activation energies recorded by Dr. Schuster are of about the same order of magnitude as those recorded by Pease in his researches with copper samples active at 0° C. when corrections were made to give the true activation energies.

¹⁴ *Z. physik. Chem.*, **12B**, 206, 1931.

Dr. Schuster's values are apparently observed activation energies. The true activation energies would be increased by the heats of adsorption of hydrogen on the active centres where hydrogenation occurs. This increase may be considerable. Would a Born-Franck mechanism be necessary in such case to explain the experimental results?

The President referred to the experiments of Dr. Ludwig Mond and his works assistant Dr. Carl Langer on the decomposition of carbon monoxide in the presence of finely divided nickel at a temperature of 350° C. When applying this process to water gas any methane or ethylene present was converted into carbon and hydrogen, the carbon-monoxide into carbon and carbon-monoxide, and the steam converting the carbon into carbon-monoxide and hydrogen.

Dr. C. Schuster (*Ludwigshafen*) said, in reply to Professor Taylor: It is suggested that in the active charcoal used for hydrogenation, the contact material consists of a few active spots on a larger inactive surface. In this respect there is no difference in the behaviour of nickel—or copper—contact materials which are prepared differently, in which cases also only a very small part of the metal surface is catalytically active the rest being inactive. From the agreement of the heats of activation of the different carbohydrates we believe that we can conclude that we have indeed measured the true heats of activation, particularly in view of the fact that Professor Taylor has calculated from the measurements of Pease on copper a low heat of activation of 4000-5000 cal.

Dr. R. W. Gurney (*Cambridge*), with regard to the paper of Dr. Butler, said: The linear relation between V and $\log i$ will cease to hold at very low overvoltages when the number of electrons making transitions to distant positive ions is no longer rapid compared with processes involving loss from the monatomic layer adsorbed on the metal surface. Electrons cannot, however, be returned to the electrode from hydrogen atoms in solution by means of the "tunnel effect"; these electron transitions through the potential barrier are unidirectional. An electron cannot in escaping from a hydrogen atom leave the proton with negative energy of hydration, since the electron transition will take place with the nucleus stationary, as in the Franck-Condon principle. We must therefore write $W=0$ in the necessary relations $E_+ < \chi - eV < \chi$, where $E_+ = I_+ - W_+$ and thus leads to $I_+ < \chi$, which is not satisfied for hydrogen atoms. The explanation of the deviation from the $\log i$ relation at overvoltages less than 0.1 volt is to be looked for in processes involving material adsorbed on the surface.

Dr. J. A. V. Butler (*Edinburgh*), in reply, said: I am quite ready to adopt Dr. Gurney's view that adsorbed hydrogen only can take part in the reverse process. Although I did not realise that it is practically impossible for hydrogen atoms *in the solution* to yield electrons to the metal at the potentials considered, and I am grateful to Dr. Gurney for pointing this out, I have always pictured the process as being due to adsorbed hydrogen. In my earlier paper I discussed explicitly the interchange of electrons between the metal and adsorbed substances, but in order to simplify the argument in this paper I wrote down the equations in a simple form, without laying stress on the adsorption stage. I should perhaps have stated more definitely that by "hydrogen atoms at the surface of the electrode," I meant to imply some kind of adsorption.

REVIEWS OF BOOKS.

"The New Conceptions of Matter." By C. G. DARWIN, M.A., F.R.S.
(London: G. Bell & Sons, Ltd., 1931. Pp. viii + 192. Price 10s. 6d.)

In this book the author aims at describing the ideas at present current about the basic constituents of the physical world. There is a clear statement of one of the greatest problems of modern physics, *viz.*, the apparent conflict of wave and corpuscular theories of light and matter. The author explains in clear and simple language how this contradiction has been removed. It is as though we had been observing for some time two different characters, a Dr. Jekyll and a Mr. Hyde. The one has a "get up" of waves, frequencies, phases and such like fancy dress with a most ingratiating personality, the other of particles, light quanta with a brusque, bullet-like bluntness. After many ingenious attempts to find the relation between these two associates, it has now been decided that they are one and the same. The illusion is due to the observer himself. Whether he sees the one or the other depends on his own spectacles. "Whatever the thing is that we call matter, it can be submitted to various experiments, some of which are devised to show wave properties, and some particle properties; but if we devise an experiment which shows the wave properties, that experiment debars us from observing the particle properties at the same time."

One of the chapters which the reviewer most enjoyed was that in which the evidence for the spin or "polarisation" of the electron is given. An analogy is drawn between the polarisation of light and the spin of the electron. The analogy is particularly striking between the deflection of atoms in the Sten-Gerlach experiment and the double refraction of light in a Nicol prism. In this way the wave aspect of the electron spin is given the necessary emphasis.

The Uncertainty Principle is discussed in some detail and numerous examples of its application are given. There is a chapter on Collisions, and it is shown that whether the collisions be between light quanta and matter, or between electrons and atoms, or between α -particles and nuclei, the same general principles apply. In the last chapter there is a description of the Exclusion Principle and of the properties of symmetry and antisymmetry in so far as they apply to electrons. It is shown how important they are in determining the properties of atoms, the electrical and magnetic properties of metals and other physical phenomena.

The book is descriptive and non-mathematical and is intended for the layman who wants to know something of the new ideas which have been introduced into physical thought. But it will appeal not only to the layman but to the specialist as well, because Professor Darwin, being a good teacher, has the art of illuminating a subject by the aptness and novelty of his illustrations.

J. E. LENNARD-JONES.

ERRATA.

Page 292 (three lines from bottom) read:—

$$1/v_1 (1 + \Delta c_1/2c_1) \Delta c_1/c_1 = 1/v_2 \cdot (1 + \Delta c_2/2c_2) \Delta c_2/c_2$$

whence
$$(1/K) \Delta c_1/\Delta c_2 = \frac{1 + \Delta c_2/2c_2}{1 + \Delta c_1/2c_1}$$

and
$$\Delta c_1/\Delta c_2 \gtrless K$$

THE INFLUENCE OF HYDROLYSED GELATINE ON THE PRECIPITATION OF SILVER CHROMATE.

BY B. N. DESAI AND G. M. NABAR.

Received 11th January, 1932.

It has been shown by various workers^{1, 2, 3} that unhydrolysed gelatin has to a very marked degree the power of retarding the appearance of a red colour in a mixture of aqueous solutions of silver nitrate and potassium chromate. Electromotive force and conductivity data² indicate that prior to the change from yellow to red the silver chromate is in solution and not in the colloidal state.⁴ Apparently a portion of the silver ion forms a supersaturated solution of silver chromate, while the remainder enters into combination with the gelatin.²

Bolam and Desai⁵ found that under comparable conditions the time which elapses before the separation of solid silver chromate decreases when the gelatin is hydrolysed by heating. Since an increase in the concentration of free silver ion would favour precipitation, the following electrometric investigation was carried out to test whether the hydrolysis decreases the combination between the gelatin and the silver.

Experimental.

The gelatin used in these experiments was a specially purified sample supplied by Messrs. Cox of Edinburgh. The moisture content was 16.35 per cent., and the ash, mainly calcium sulphate, 1.18 per cent. Since it has been shown² that calcium has no effect on the precipitation, no attempt was made to render the gelatine ash-free.

The gelatin was hydrolysed by heating a 3 per cent. solution in a fused silica flask (with a water-cooled reflux condenser) on a water bath at 100°. The flask and its contents were weighed before and after each period of heating and any loss (which was always small) was made good by the addition of conductivity water.

The activity of the silver ion in the chromate mixtures was determined by means of a cell of the type



where X denotes the solution of silver chromate with or without other electrolytes or gelatin. The cell was kept at a temperature of $30^\circ \pm 0.1^\circ \text{C}$. Before each experiment the silver gauze electrode was carefully cleaned and electroplated. Its constancy was tested by

¹ Williams and Mackenzie, *J. Chem. Soc.*, 117, 844, 1920.

² Bolam and Mackenzie, *Trans. Far. Soc.*, 22, 151, 162, 1926.

³ Hedges and Henley, *J. Chem. Soc.*, 2714, 1928.

⁴ Chatterjee and Dhar, *Trans. Far. Soc.*, 23, 23, 1927; *J. Indian Chem. Soc.*, 5, 175, 1928.

⁵ Bolam and Desai, *Trans. Far. Soc.*, 24, 50, 1928.

measurements in a pure solution of silver nitrate, and it was found that the potential did not vary with time. The potential of the silver electrode in a saturated solution of silver chromate was determined and the observed value agreed quite satisfactorily with the calculated value.

In the precipitation experiments 5 c.c. of (say) $N/100$ AgNO_3 + 3.7 c.c. of 3 per cent. gelatin and 5 c.c. of $N/100$ K_2CrO_4 + 3.7 c.c. of 3 per cent. gelatin were mixed, after allowing the separate solutions to attain a temperature of 30°C . The mixture was immediately transferred to the electrode vessel, which was kept in the thermostat, and the potential developed by the silver electrode measured from time to time.

The activity of the silver ion was calculated from the equation

$$E = E_0 - \frac{RT}{nF} \ln a_{\text{Ag}^+},$$

where E_0 was calculated from data given by Lewis and Randall.⁶ E , the observed *e.m.f.*, for Ag/AgNO_3 was found to be within 0.16 per cent. of the calculated value.

Results and Discussion.

Table I. contains the initial and final values, as well as the differences between them, of the activity of the silver ion in the reacting mixtures containing different concentrations of the reactants in gelatin hydrolysed

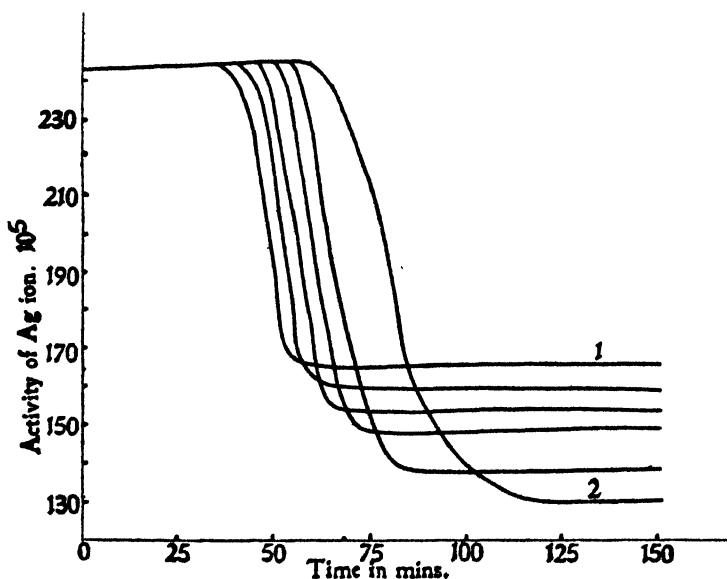


FIG. 1.— $0.01\text{ }N$ AgNO_3 + $0.01\text{ }N$ K_2CrO_4 + gelatine.
1 = 10 hours hydrolysis. 2 = No hydrolysis.

to different extents. The values of the activity of the silver ion at different times after mixing the solutions in the case of $0.01\text{ }N$ AgNO_3 + $0.01\text{ }N$ K_2CrO_4 + gelatin have been plotted in Fig. 1. Similar curves were obtained for the other systems.

⁶ Lewis and Randall, *Thermodynamics*, 1923.

It will be seen that the activity remained constant for some minutes, then rapidly decreased and finally became constant. It was noted that there was no further change even after six hours. The point at which the activity commenced to fall corresponded in every case with the first appearance of a red colour. Until this point was reached the mixture remained clear yellow. It is evident that our experiments support the conclusion of Bolam and Mackenzie² that the red colour is due to the precipitation of the silver chromate from true solution, and is not the result of the coagulation of a sol of silver chromate.

If the time required for the appearance of the precipitate is taken as a measure of the inhibitive power of the gelatine, it appears that the efficiency of the gelatine in this respect is the lower the longer the gelatin is hydrolysed. This is in agreement with the observations of Bolam and Desai.⁵

Table I. and the curves show that the initial value * of the activity

TABLE I.

Gelatine Dispersed at 35° C. and Hydrolysed for		Concentration of Reactant.									
		0.01 N AgNO ₃ , 0.01 N K ₂ CrO ₄ .		0.01 N AgNO ₃ , 0.011 N K ₂ CrO ₄ .		0.01 N AgNO ₃ , 0.012 N K ₂ CrO ₄ .		0.011 N AgNO ₃ , 0.01 N K ₂ CrO ₄ .		0.012 N AgNO ₃ , 0.01 N K ₂ CrO ₄ .	
		Initial Activity of Ag ion × 10 ⁶ . 243.						Initial Activity of Ag ion × 10 ⁶ . 280.		Initial Activity of Ag ion × 10 ⁶ . 317.	
		Final Activity of Ag ion × 10 ⁶ .	Difference × 10 ⁶ .	Final Activity of Ag ion × 10 ⁶ .	Difference × 10 ⁶ .	Final Activity of Ag ion × 10 ⁶ .	Difference × 10 ⁶ .	Final Activity of Ag ion × 10 ⁶ .	Difference × 10 ⁶ .	Final Activity of Ag ion × 10 ⁶ .	Difference × 10 ⁶ .
Hrs.											
0	130	113	120	123	105	138	128	152	133	184	
2	139	104	125	118	116	127	145	135	150	167	
4	149	94	137	106	123	120	157	123	160	157	
6	154	89	143	100	128	115	165	115	167	150	
8	160	83	149	94	135	108	174	106	177	140	
10	166	77	154	89	139	104	179	101	183	134	

was unaffected by the hydrolysis of the gelatin. The greater tendency to precipitation brought about by heating the gelatine cannot, therefore, be ascribed to an increase in the concentration of the free silver ions.

A striking feature of the results is that the final value of the activity increases with increase in the hydrolysis, although precipitation takes place more readily. At present it is difficult to suggest an explanation of this effect and the matter requires further investigation.

The p_H of the gelatin at various stages of hydrolysis was determined colorimetrically and the values are given in Table II.

While increase in the p_H would, on the one hand, tend to favour precipitation, on the other it might be expected to promote combination

* The initial value was the same as the value of the activity obtained when the silver nitrate alone was present in the gelatin solution. In agreement with previous experience it was found that the gelatin produced an appreciable decrease in the activity of the silver ion.

TABLE II.

Treatment of Gelatin.	pH.
Dispersed at 35° C. . . .	5.15
Heated for—	
6 hours	5.25
8 „	5.30
12 „	5.40

between the gelatin and the silver ion (see Bolam and Mackenzie).² It is thus all the more surprising that the final value of the activity increases with the hydrolysis.

The authors wish to thank Prof. A. R. Normand for his constant interest and some valuable suggestions, and Dr. T. R. Bolam (*Edinburgh*) for helpful criticism.

Note by Referee.—It should be mentioned that Liesegang quite clearly realised an effect of gelatose (hydrolysed gelatin) on the precipitation of silver chromate and more particularly on the formation of rings.⁷

⁷ R. E. Liesegang, *Z. physik. Chem.*, 88, 1, 1914.

*Physical Chemistry Laboratory,
Wilson College,
Bombay 7, India.*

THE α AND β SOLID SOLUTIONS OF THE COPPER-ZINC ALLOYS AND THE CORRESPONDING LIQUID SOLUTIONS IN EQUILIBRIUM WITH THEM EXAMINED THERMODYNAMICALLY.

BY F. H. JEFFERY.

Received 21st January, 1932.

The following attempt of thermodynamic analysis is based on the work of Genders and Bailey¹ for the boundary separating the α solid solution phase from the mixed α and β phases and for the determination of the point where this meets the 905° isothermal, on the work of Matthewson and Davidson² for the boundary separating the mixed α and β phases from the β solid solution, and on the work of Parravano³ for the liquidus and solidus bounding the liquid solution which gives the α solid solution.

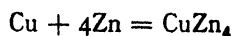
For the α solid solution and for the liquid solution from which it is derived it was found that the boundary conditions could be satisfied by the assumption that all the zinc is combined with copper in the liquid, and exists as a compound in solution with the rest of the copper, and

¹ Genders and Bailey, *J. Inst. Metals*, 33, 213, 1925.

² Matthewson and Davidson, *J. Amer. Inst. Metals*, 11, 12, 1917.

³ Parravano, *Gazz. chim. ital.*, 44, 478, 1914.

that the solid solution is of the same nature. It appeared that when zinc dissolves in liquid copper the following reaction—



takes place.

If both liquid and solid solutions consist of CuZn_4 dissolved in Cu the thermodynamic equations must be of the form—

$$\log (1 - n') - \log (1 - n) = \log K$$

and

$$\frac{\partial}{\partial \theta} \log K = - \frac{\lambda}{R\theta^2}$$

Hence for dilute solutions for which λ is sensibly constant for the formation of the solid solution from the liquid, within the range of temperature and concentration used,

$$\log (1 - n') - \log (1 - n) = \frac{\lambda}{R\theta} + \text{constant.}$$

The results obtained are shown in the following table :—

θ .	Per Cent. Zn in Liquid.	Per Cent. Zn in Solid.	n .	n' .	$1/\theta$.	$\log (1 - n') - \log (1 - n)$.
1343	2.5	1.7	6.23×10^{-3}	4.20×10^{-3}	7.446×10^{-4}	0.089×10^{-3}
1333	5.0	3.0	12.8	7.52	7.502	0.232
1323	7.5	4.5	19.7	11.5	7.559	0.364
1313	10.0	6.0	27.0	15.5	7.616	0.510
1303	12.5	7.7	34.7	20.3	7.675	0.645
1293	15.0	9.5	42.9	25.5	7.734	0.781
1283	17.5	11.5	51.6	31.6	7.794	0.905
1273	20.4	13.7	62.3	38.6	7.856	1.084

If $\log (1 - n') - \log (1 - n)$ be plotted as a function of $1/\theta$ these points lie on a straight line through the second and the sixth. The mean value of $\lambda = 1081$.

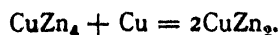
This line should pass through the point given by $n = n' = 0$ and $\theta = 1356$. It is proximate to the point but it seems that it should be closer unless there is some small persistent error in the temperature determinations given by Parravano.

These results lead to the conclusion that both liquid and solid phases are solutions of CuZn_4 in monatomic Cu molecules.

There seems no reason to suppose that there is any discontinuity in the liquid phase at 905°C .; the liquid phase in equilibrium with the mixed α and β phases and with the β phase appears to be a solution of CuZn_4 in Cu.

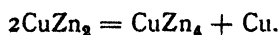
The phase boundaries separating the α solid solution from the mixed α and β phases and this latter from the β solid solution both slope in the same direction, indicating increasing zinc concentration with decreasing temperature for both α and β . Pure β when it cools gives rise to α and a β solid solution richer in zinc than that from which this latter is derived.

The boundary conditions can be satisfied if β be a solid solution of CuZn_4 in monatomic Cu. If this be so, β is formed from the liquid phase in equilibrium with it by the reaction



454 SOLID SOLUTIONS OF THE COPPER-ZINC ALLOYS

And when β cools α must be formed by the reaction



The corresponding thermodynamic equation is

$$\nu \log n + \nu_0 \log (1 - n) + \nu' \log n' + \nu'_0 \log (1 - n') = \log K,$$

where

$$\nu = -2, \quad \nu_0 = 0, \quad \nu' = 1, \quad \nu'_0 = 1,$$

hence

$$-2 \log n + \log n' + \log (1 - n') = \log K,$$

and therefore provided the solid solutions are sufficiently dilute and that the heat of reaction is sensibly constant for the range of temperature and concentration examined,

$$-2 \log n + \log n' + \log (1 - n') = \frac{\lambda}{R\theta} + \text{constant}.$$

The results obtained are shown in the table following :—

θ .	Per Cent. Zinc in β .	Per Cent. Zinc in α .	n .	n' .	$-2 \log n$ + $\log n'$ + $\log (1 - n')$.	$1/\theta$.
1153	37.7	33.0	2.94×10^{-1}	1.20×10^{-1}	0.855×10^{-1}	8.673×10^{-4}
1125	38.2	33.5	3.01	1.22	0.755	8.889
1103	38.6	34.0	3.06	1.25	0.691	9.066
1073	39.2	34.5	3.14	1.28	0.554	9.322
1043	39.8	35.0	3.21	1.31	0.418	9.588

The points lie on a straight line through the first and the fourth. The mean value of $\lambda = -2141$.

This leads to the conclusion that the β solid solution consists of the compound CuZn_2 dissolved in monatomic molecules of Cu.

The high concentrations of CuZn_2 in the β solid solution for which the thermodynamic equation is applicable are noteworthy. There does not appear to be any "*point saillant*" on either of these two sloping boundaries of the mixed α and β phases from 905° to 550° , hence the β solid solution must have the constitution given above for a range of temperature down to at least 550° .

Discussion of these Results.

1. The liquid solutions in equilibrium with the α and β solid solutions appear to be CuZn_4 dissolved in monatomic molecules of copper. This result implies that when zinc is dissolved in molten copper the compound CuZn_4 is formed and dissolves in the excess of copper present. The author found that when tin was dissolved in molten copper Cu_4Sn was formed and dissolved in excess of copper.

2. The α solid solution appears to be a solution of CuZn_4 in monatomic molecules of copper.

3. The β solid solution appears to be a solution of CuZn_2 in monatomic molecules of copper.

4. The complexity of these liquid and solid solutions seems consistent with the formation of metastable states.

5. X-ray analysis of the copper-zinc system and of the copper-tin system indicates the similarity of structure of the α solid solution phases of these systems and also the similarity of structure of the β solid solutions.

The α phase of the Cu-Sn system is, according to the author,⁴ a solid solution of Cu_4Sn in Cu; the α phase of the Cu-Zn system is CuZn_4 in Cu according to the author. It seems difficult to see that these are of similar constitution, bearing in mind that the solvent is copper in both cases.

The β phase of the Cu-Sn system is, according to the author, a solid solution of tin in copper; and according to the author the β phase of the Cu-Zn system is CuZn_2 in Cu. Again it seems that there is little similarity.

Westgren and Phragmén⁵ state that the β -phases of the systems Cu-Zn and Cu-Sn are analogous in structure, and that this has been confirmed by X-ray investigations: they qualify this statement by writing: "in each case the atoms occupy the points of a body-centered cubic lattice . . . but in β Cu-Zn the different kinds of atoms are mainly orientated in networks of their own, forming what may be denominated 'super-lattices.' "

If the thermodynamic equations be correct the compounds Cu_4Sn , CuZn_4 , CuZn_2 must maintain their identity in solid solution in Cu. The three-dimensional pattern of CuZn_2 dissolved in monatomic Cu can hardly be as simple as that of monatomic Sn dissolved in monatomic Cu.

⁴ Jeffery, *Trans. Faraday Soc.*, **27**, 136, 1931.

⁵ Westgren and Phragmén, *Trans. Faraday Soc.*, **25**, 380, 1929.

*The Goldsmiths' Metallurgical Laboratory,
Cambridge.*

THE CONSTITUTION OF THE LIQUID AND SOLID ALLOYS OF THE COPPER-GOLD SYSTEM EXAMINED THERMODYNAMICALLY.

BY F. H. JEFFERY.

Received 11th February, 1932.

The thermal equilibrium diagram of this system has been investigated by N. S. Kurnakow and S. F. Zemczuzny.¹ They found it to be of the Roozeboom type 3, with a minimum at 884° and 40.5 atomic per cent. copper. They found that the solid solution gave rise to the compounds CuAu at 367° and Cu_3Au at 371° . It seems interesting to examine whether the liquid or solid solution contains a compound, as appears to be the case with the α solid solution of Sn in Cu and the liquid in equilibrium with it, and also with the α solid solution of Zn in Cu and the liquid in equilibrium with it.² Failing this, these compounds must be formed at more than 500° below the temperature of the minimum on

¹ Kurnakow and Zemczuzny, *Z. anorg. Chem.*, **54**, 162, 1907, and *J. Inst. Metals*, **15**, 305, 1916.

² Jeffery, *Trans. Faraday Soc.*, **27**, 136, 1931.

the solidus by the direct combination of the copper and gold existing together in solid solution.

The numbers used for the following calculations were taken from the 1907 paper of Kurnakow and Zemczuzny; they stated that they had verified these results for the liquidus and solidus in their further investigations of 1916.

The simplest assumption as to the molecular constitution of the liquid and solid solutions is that the components of each are monatomic molecules of copper and of gold. If n be the molal fraction of gold in copper in the liquid phase and n' that in the solid phase—

$$-\log(1-n) + \log(1-n') = \lambda/R\theta - \lambda/R\theta_0$$

θ_0 being the freezing-point of copper, λ being sensibly constant for the range of temperature and concentration examined. Inasmuch as the determination of the solidus in a system of this type is difficult, calculations have been made for alloys freezing at temperatures separated by intervals of five degrees and have been continued until the assumption as to the constancy of λ became incompatible with the concentration of the solutions as determined by the diagram. The results shown in the table were obtained—

θ .	Atomic Per Cent. Au in Liquid.	Atomic Per Cent. Au in Solid.	$-\log(1-n).$ $+\log(1-n').$	$1/\theta$.
1356	0	0	0×10^{-3}	7.375×10^{-4}
1348	1.5	0.6	0.395	7.418
1343	2.6	1.0	0.708	7.446
1338	3.5	1.4	0.935	7.474
1333	4.4	1.9	1.121	7.502
1328	5.2	2.3	1.308	7.530
1323	6.4	2.8	1.639	7.558
1318	7.4	3.4	1.837	7.587
1313	8.4	3.9	2.082	7.616
1308	9.5	4.5	2.335	7.645
1303	10.4	5.0	2.541	7.675
1298	11.4	5.7	2.708	7.704

These points lie on the straight line through the point $n = n' = 0$, $\theta = 1356$, and the tenth point.

Calculations for solutions of copper in gold using an equation of the same form, θ_0 being the freezing-point of gold, n the molal fraction of copper in the liquid solution and n' that in the solid solution, gave the following results:—

θ .	Atomic Per Cent. Cu in Liquid.	Atomic Per Cent. Cu in Solid.	$-\log(1-n).$ $+\log(1-n').$	$1/\theta$.
1336	0	0	0×10^{-3}	7.485×10^{-4}
1328	1.4	0.5	0.394	7.530
1323	2.2	0.9	0.573	7.558
1318	3.0	1.4	0.711	7.587
1313	3.9	1.8	0.939	7.616
1308	4.8	2.4	1.081	7.645
1303	5.6	2.8	1.270	7.675
1298	6.4	3.4	1.370	7.704
1293	7.3	3.9	1.564	7.734

These points lie on the straight line through the second and the seventh. This straight line should pass accurately through the point $n = n' = 0$, $\theta = 1336$: this point is close to the line but should be closer; probably this is due to a small persistent error in the determination of the solidus temperatures.

These results lead to the conclusion that both the liquid solution and the solid solution are derived from monatomic molecules of copper and monatomic molecules of gold.

Calculations were also made on the assumption that one or other of the compounds CuAu , Cu_3Au was present in either of the solutions or in both, inasmuch as the same compound could not be present in both solutions simultaneously there are six possibilities. In all these cases the results were altogether inconsistent with the boundary conditions. This confirms the simple constitution of the liquid and solid solutions.

*The Goldsmiths' Metallurgical Laboratory,
Cambridge.*

ANODE PHENOMENA IN THE ELECTROLYSIS OF POTASSIUM ACETATE. PART III. FORMATION OF METHANE.

BY SOORYA N. SHUKLA AND OSWALD J. WALKER.

Received 25th January, 1932.

It has recently been shown that under certain conditions appreciable quantities of methane are formed at a smooth platinum anode during the electrolysis of aqueous potassium acetate solutions, and that the conditions favourable for the formation of that hydrocarbon appear to be low current density and high concentration of acetate.¹ In a further investigation of the conditions favourable for methane formation the effect of (1) the nature of the solvent, and of (2) the nature of the anode material has been examined. Some further experiments on the electrolysis of aqueous solutions with a smooth platinum anode are also described.

Electrolysis of Potassium Acetate in Non-Aqueous Solvents.

When solutions of potassium acetate in methyl alcohol, in ethyl alcohol and in acetic acid are electrolysed at ordinary current densities the current efficiency for the Kolbe reaction by which ethane is formed may become as high as 95-97 per cent.² Solutions of potassium acetate in these solvents were electrolysed at low current densities in order to see whether methane could be obtained under these conditions.

The electrolyses were carried out in an H-shaped glass vessel at 20° C. as before, but since organic solvents were to be used, all rubber connections and stoppers were replaced by glass joints. The solvents were purified and dried, and a 10 per cent. by weight solution of potassium acetate made up and refluxed to get rid of dissolved air. The access of

¹ *Trans. Far. Soc.*, **27**, 35 and 722, 1931; referred to as Parts I. and II.

² Salauze, *Bull. Soc. Chim.*, **37**, 522, 1925.

air to the solution during the electrolysis was prevented as far as possible. The anode was a smooth platinum wire of 1.38 sq. cm. surface area, and the cathode a smooth platinum foil. Collection of the anode gases was started when the current had reached a steady value, and the mixture was analysed as described previously. A series of electrolyses of a 10 per cent. aqueous solution of potassium acetate (containing an equivalent amount of added acetic acid) were carried out in the same vessel, and under similar conditions in order to provide more comparable data.

The results are given in Table I. in the last column of which the values of the ratio $\text{CH}_4/\text{C}_2\text{H}_6$ are shown. It will be seen that in all cases considerable amounts of methane are formed at low-current densities, and that the ratio of methane to ethane decreases with increasing *C.D.* Qualitatively, and in a rough quantitative manner also, the composition of the anode gases obtained from aqueous and non-aqueous solutions is the same. In the case of acetic acid as solvent a *N* solution of the acetate was electrolysed at lower *C.D.*, using a large

TABLE I.

Solvent.	C.D. milli-amp./ cm ² .	Percentage Composition of Anode Gas.						Ratio $\text{CH}_4/\text{C}_2\text{H}_6$.
		CO_2 .	O_2 .	CO .	C_2H_6 .	CH_4 .	Residue.	
CH_3COOH	0.72	59.5	0.5	1.2	32.1	4.7	2.0	0.15
	2.17	61.0	0.7	1.1	33.2	2.6	1.4	0.08
	3.61	61.9	0.7	1.4	33.3	1.7	1.0	0.04
	5.78	59.6	0.4	1.2	35.8	1.8	1.2	0.05
	7.22	59.2	0.6	0.8	36.5	1.4	1.5	0.04
	10.82	58.9	0.7	1.0	36.5	1.6	1.3	0.04
CH_3OH	0.72	41.8	1.1	2.0	31.1	14.3	9.7	0.46
	2.17	57.7	1.4	1.4	35.1	2.4	2.0	0.07
	3.61	59.5	0.6	0.9	34.5	2.6	1.9	0.08
	5.78	60.4	0.4	0.9	35.4	1.7	1.2	0.05
	7.22	58.3	0.3	1.0	37.1	1.8	1.5	0.05
	10.82	57.9	0.7	1.1	37.7	0.6	2.0	0.02
$\text{C}_2\text{H}_5\text{OH}$	0.72	51.3	0.8	1.1	25.6	18.9	2.3	0.74
	1.80	62.6	0.8	1.0	23.8	11.0	0.8	0.46
	2.17	57.5	0.5	1.2	29.1	10.7	1.0	0.37
	3.61	55.2	0.6	1.0	31.6	10.3	1.3	0.33
	5.78	54.8	0.8	1.1	35.6	6.1	1.3	0.17
	7.22	54.4	0.7	1.0	35.9	6.5	1.5	0.18
H_2O	10.82	56.6	1.4	1.4	34.4	4.2	2.0	0.12
	0.72	54.0	38.8	2.1	0	0	5.1	—
	1.08	52.4	43.3	2.9	0	0	1.4	—
	1.26	65.6	2.9	2.1	11.8	15.8	1.8	1.35
	1.30	71.5	1.2	1.9	12.2	12.5	0.5	1.03
	1.44	71.1	1.1	1.3	19.1	7.1	0.2	0.37
	2.17	70.0	0.7	1.0	23.7	4.3	0.3	0.18
	3.61	66.9	0.5	1.1	27.5	3.4	0.6	0.14
	5.78	66.6	0.6	1.1	28.5	2.5	0.7	0.09
	7.22	64.9	0.8	1.0	30.5	2.2	0.6	0.07
	10.82	57.3	0.7	0.9	38.0	2.0	1.1	0.05

foil anode (14 sq. cm. surface area), and the following values of the $\text{CH}_4/\text{C}_2\text{H}_6$ ratio were obtained:—

C.D.	0.036	0.071	0.19	0.36
$\text{CH}_4/\text{C}_2\text{H}_6$	3.33	1.43	0.84	0.69

These values are of the same order as those obtained with aqueous solutions.

In the case of the aqueous solutions the $\text{CH}_4/\text{C}_2\text{H}_6$ ratio affords a convenient measure of the extent to which these two hydrocarbons are formed under specified conditions, but in the non-aqueous solvents the composition of the anode gas will undoubtedly be affected by the increased solubility of methane and of ethane. Moreover, in the alcohols ethane is about five times more soluble than methane. In these cases, therefore, too much importance must not be attached to the actual values of the $\text{CH}_4/\text{C}_2\text{H}_6$ ratio.

It is of interest also to compare the current efficiency for the formation of methane with different solvents. In the following table the values of the CH_4/H_2 ratio, *i.e.*, the ratio of the volume of methane evolved at the anode to the volume of hydrogen evolved at the cathode, are compared for the region of *C.D.* in which the $\text{CH}_4/\text{C}_2\text{H}_6$ ratio varies rapidly during the electrolysis of 10 per cent. solutions of potassium acetate in (a) water, and (b) acetic acid. The corresponding values of the $\text{C}_2\text{H}_6/\text{H}_2$ ratio are also shown. The decrease in the $\text{CH}_4/\text{C}_2\text{H}_6$ ratio with increasing *C.D.* is due mainly to the increasing current efficiency for ethane formation.

TABLE II.

Solvent.	<i>C.D.</i> Milliamps./sq. cm.	$\text{CH}_4/\text{C}_2\text{H}_6$	$\text{C}_2\text{H}_6/\text{H}_2$	CH_4/H_2
Water	1.26	1.35	0.068	0.092
	1.81	0.29	0.32	0.090
	3.61	0.13	0.60	0.075
Acetic acid	0.11	0.91	0.18	0.17
	0.21	0.52	0.37	0.19
	0.36	0.34	0.57	0.19
	0.71	0.27	0.23	0.061

Nature of the Anode Material.

The electrosynthesis of ethane from acetate in aqueous solution is dependent on the nature of the anode material. For example, ethane formation occurs readily at smooth platinum, iridium, and graphite electrodes, whereas at platinised platinum and gold anodes the gas evolved consists mainly of oxygen and carbon dioxide. In the non-aqueous solvents considered in the preceding section, however, the nature of the anode, provided it is not attacked, has much less influence than in aqueous solution,³ *e.g.*, synthesis takes place readily at a gold anode in glacial acetic acid solution.

In the following experiments aqueous solutions of potassium acetate were electrolysed at 20° C. with anodes of iridium, graphite, and gold of surface area 1.38, 7.0, and 1.38 sq. cm., respectively. A 3.5 *N* solution was used, since with this solution the largest $\text{CH}_4/\text{C}_2\text{H}_6$ ratios were obtained with the smooth platinum anode.

With the gold anode no hydrocarbons were formed at any *C.D.* within the range employed, *viz.*, 0.72-700 milliamps/sq. cm. The anode gas consisted of oxygen with 20-40 per cent. of carbon dioxide. The anode is attacked, especially at the higher *C.D.* and the solution becomes dark-coloured by the dispersed gold.

With the iridium and graphite anodes, however, the composition of the gas evolved is very similar to that obtained with a smooth platinum

TABLE III.

Current Density Milliamps./sq. cm.	Percentage Composition of Anode Gases.						Ratio. CH ₄ /C ₂ H ₆ .
	CO ₂ .	O ₂ .	CO.	C ₂ H ₆ .	CH ₄ .	Residue.	
Graphite anode							
0.71	78.0	0.5	1.4	5.4	13.9	0.8	2.57
1.43	77.1	0.6	1.0	5.3	15.4	0.6	2.89
2.14	73.7	0.5	0.9	6.2	18.5	0.2	2.97
3.57	69.1	0.4	0.7	9.2	20.6	0	2.23
5.71	68.5	0.4	0.9	11.4	18.5	0.3	1.63
7.14	65.5	0.5	1.3	18.7	13.8	0.2	0.74
17.9	70.0	0.5	1.7	23.8	3.5	0.5	0.15
Iridium anode							
0.65	35.5	1.2	1.5	35.5	24.3	2.0	0.68
0.72	53.5	0.8	1.3	32.2	11.5	0.7	0.36
1.44	60.5	0.5	1.0	32.5	4.6	0.7	0.14
2.16	60.7	0.5	0.9	33.7	3.4	0.8	0.10
3.61	59.6	0.5	1.1	35.7	2.2	0.9	0.06
7.22	61.3	0.3	0.9	35.3	1.5	0.7	0.04

anode, and at low *C.D.*'s quite appreciable amounts of methane are formed. The results of the gas analyses are given in Table III. By comparing these results with the corresponding data for a smooth platinum anode in Part II. (Table III.), it is seen that qualitatively all three electrodes behave in a similar manner. A quantitative comparison of the specific effect of different anodes on the methane reaction cannot be obtained simply from an inspection of the values of the $\text{CH}_4/\text{C}_2\text{H}_6$ ratio, since this ratio is dependent on the effect of the anode material on the ethane synthesis also. This can be done, however, by comparing the values of the CH_4/H_2 ratio, which affords a measure of the current efficiency for the formation of methane. In the following table the data for the electrolysis of the 3.5 *N* solution with platinum and iridium anodes are compared for the range of *C.D.* 0.72-7.2 milliamps./sq. cm.

TABLE IV.

<i>C.D.</i>	CH_4/H_2 , Platinum.	CH_4/H_2 , Iridium.
0.72	0.21	0.10
2.17	0.14	0.067
3.61	0.12	0.044
7.22	0.053	0.032

Within this range of *C.D.* the current efficiency for the formation of methane at a platinum anode is approximately double that at an iridium anode. In both cases, however, the amount of methane formed decreases with increasing *C.D.*

Variation of the Concentration of Free Acetic Acid.

In examining the effect of the concentration of acetate on the formation of methane during the electrolysis of aqueous solutions, an equivalent amount of acetic acid was added to the solution in order to keep it acid. The effect of varying the acidity of the solution by adding varying amounts of acetic acid or of potassium hydroxide to a solution which was kept 1.0 *N* throughout with respect to potassium acetate can be seen from the following table, in which the values of the $\text{CH}_4/\text{C}_2\text{H}_6$ ratio at approximately 2.1 and 3.6 milliamps./sq. cm. are compared :—

TABLE V.

Electrolyte.	$\text{CH}_4/\text{C}_2\text{H}_6$.	
	2.1 milliamps./sq. cm.	3.6 milliamps./sq. cm.
1.0 <i>N</i> CH_3COOK + 3.5 <i>N</i> CH_3COOH	0.21	0.11
" + 1.0 <i>N</i> "	0.37	0.15
" + 0.5 <i>N</i> "	0.34	0.14
" + 0 "	0.49	0.18
" + 0.1 <i>N</i> KOH	0.63	0.21
" + 0.5 <i>N</i> "	—	—

The variation of the acetic acid concentration has only a small effect compared with that of varying the acetate concentration. The $\text{CH}_4/\text{C}_2\text{H}_6$ ratio tends to increase with decreasing acidity of the solution. If the latter is made not too strongly alkaline the ratio is still further increased, due to the Hofer and Moest reaction having commenced at the expense of the ethane synthesis. With 0.5 *N* KOH , however, no hydrocarbons are evolved.

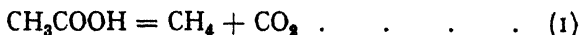
Mechanism of Methane Formation.

It has been shown in this paper and the two preceding papers that methane may be formed at the anode during the electrolysis of potassium acetate solutions under very varying conditions when the anodic current density is low. The question naturally arises, What is the nature of the reaction by which this hydrocarbon is formed? It must be admitted that the experiments described so far do not provide any definite answer. Before a more detailed study has been made of the anode processes under the conditions most favourable for the formation of methane any suggestions regarding the mechanism of its formation must be somewhat speculative, and we do not propose, therefore, to enter into a detailed discussion of the possible reactions at this stage. There is, however, one possibility which deserves being mentioned, and which may form the basis of further investigation.

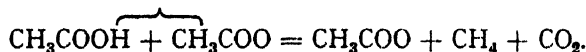
In the first place, it is necessary to emphasise again the almost general occurrence of methane as a decomposition product of acetic acid or of its salts and derivatives. In particular, mention must be made of two reactions in which both methane and ethane are formed, the proportions of the two hydrocarbons depending on the experimental conditions. Baur and Rebmann⁴ showed that in the photolysis of acetic acid in

⁴ *Helv. Chim. Act.*, **5**, 221, 1922.

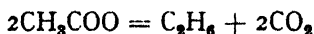
presence of uranyl salts two distinct processes take place, *viz.*, (1) a photocatalytic decomposition of acetic acid into methane and carbon dioxide



and (2) an oxidation of the acetate ion into ethane and carbon dioxide. Gordon ⁵ found that when a solution containing sodium persulphate and acetic acid or sodium acetate is heated, a mixture of gases is evolved, consisting of carbon dioxide, methane and ethane, and that the formation of methane is favoured by a high concentration of sodium acetate. He also assumed a catalytic decomposition of acetic acid according to (1), accompanied by an oxidation to ethane and carbon dioxide. The catalytic decomposition of acetic acid into methane and carbon dioxide can also occur in other ways, *e.g.*, when acetic acid is passed over reduced nickel at 210°, ⁶ or over silica gel at 430-460°. ⁷ It is possible, therefore, that a reaction of this kind is taking place at the anode during the electrolysis of the acetate, *e.g.*, by the action of an acetate radical on a molecule of acetic acid, as follows



The net result of this reaction is a decomposition of acetic acid as in (1). With increasing *C.D.* and consequent increase in the concentration of acetate radicals at the anode surface, the tendency for the reaction



to occur increases, and therefore the ratio of methane to ethane decreases. At any rate, it does seem probable that methane is being formed by a very similar process in the electrolytic reaction and in the reactions described by Baur and by Gordon.

Summary.

(1) Methane is formed at the anode during the electrolysis at low current densities of solutions of potassium acetate in acetic acid, in methyl alcohol, and in ethyl alcohol.

(2) In aqueous solution methane is also formed at anodes of iridium and of graphite.

In conclusion, one of us (S. N. S.) wishes to thank the Government of the United Provinces of Agra and Oudh, India, for a research scholarship during the tenure of which the work described in this and the two preceding papers has been done.

⁵ *J. Physical Chem.*, **18**, 55, 1914.

⁶ Sabatier and Senderens, *Ann. Chim.* [8], **4**, 476.

⁷ Mitchell and Reid, *J. Amer. Chem. Soc.*, **53**, 338, 1931.

STUDIES IN GELS III.

VAPOUR PRESSURE OF SILICA GELS.

BY D. G. R. BONNELL.

Received 1st February, 1932.

A review of the literature on the absorption of aqueous vapour by silica gels shows that this subject has been very carefully studied. One of the earliest investigators was van Bemmelen,¹ who determined the sorption and desorption curves for silica gels in contact with aqueous vapour. Anderson,² Zsigmondy,³ and others have investigated the problem further, and their general experimental conclusions were similar to those arrived at by van Bemmelen. Notwithstanding the large number of investigations, all the information available concerns the dialysed gel only, *i.e.*, gels which were treated to remove the electrolytes formed during preparation before being investigated. The writer is not conversant with any work done on undialysed gels, *i.e.*, those containing electrolyte. The following experiments were carried out in an endeavour to throw some light on the relative behaviour of dialysed and undialysed gels prepared from sodium silicate by hydrochloric, sulphuric and acetic acids.

Experimental.

The apparatus used was a slight modification of that described by Bachmann⁴ and is shown diagrammatically in Fig. 1.

The main part is equipped with three high-vacuum stopcocks, S_1 , S_2 , S_3 , and a manometer M. Below S_1 , a flask A is connected by a ground joint J_1 , while below S_3 , a flask B, of pattern shown, is joined in like manner by J_2 . These flasks can be held in position by means of strong rubber bands fitting over the glass protuberances *a a*₁, and *b b*₁. The ground joints J_1 and J_2 are of a standard size, enabling several flasks of B pattern to be used for the same apparatus.

In order to facilitate the diffusion of vapour, the connecting tubes and stopcocks were made of 1 cm. bore.

Method of Procedure.

The apparatus was connected together and evacuated to about 1/100 mm. pressure by means of a Hyvac rotary oil pump connected to S_2 . This low pressure was maintained until no increase was registered on allowing the apparatus to stand for 24 hours after closing S_2 . The tap T was then closed, B removed, cleaned from all adhering grease on the ground joint and weighed. After the introduction of dry air B was reweighed, a quantity of the gel under investigation introduced, and the whole again weighed. The latter two weighings give the weight of the gel employed. B was reconnected to the apparatus, evacuated and, as a precaution, again removed and weighed.

For the desorption or drying curve, S_1 was closed and a part of the water in the gel carefully removed by evacuation. With S_2 closed the

¹ van Bemmelen, *Z. anorg. allg. Chem.*, **13**, 233, 1897; **18**, 98, 1898.

² Anderson, *Z. physik. Chem.*, **88**, 191, 1914.

³ Zsigmondy, *Z. anorg. allg. Chem.*, **71**, 356, 1911.

⁴ Bachmann, *Z. anorg. allg. Chem.*, **168**, 63, 1927. See also Thiessen, *Z. anorg. allg. Chem.*, **180**, 65, 1929.

system was allowed to attain equilibrium and the pressure exerted by the gel at this point obtained from the manometer. After closing T, B was removed and weighed. This procedure was repeated at intervals down to zero pressure.

For the sorption or wetting curve, 100 c.c. of distilled water was introduced into A. The whole apparatus was evacuated—with T closed—until the water boiled and removed the traces of air left. By first closing S_1 , evacuating and then opening S_1 while S_2 was closed, the whole apparatus external to B was filled with aqueous vapour up to saturation pressure. Closing S_1

and opening T allowed the gel to absorb moisture until equilibrium was attained, the pressure at the latter point being read from the manometer. At this point B was removed and weighed as before. The whole procedure was repeated until the equilibrium pressure equalled the saturation pressure of water.

With this method the quantity of water added to the gel can be controlled.

The gels investigated were prepared from sodium silicate and acids of the same degree of purity as

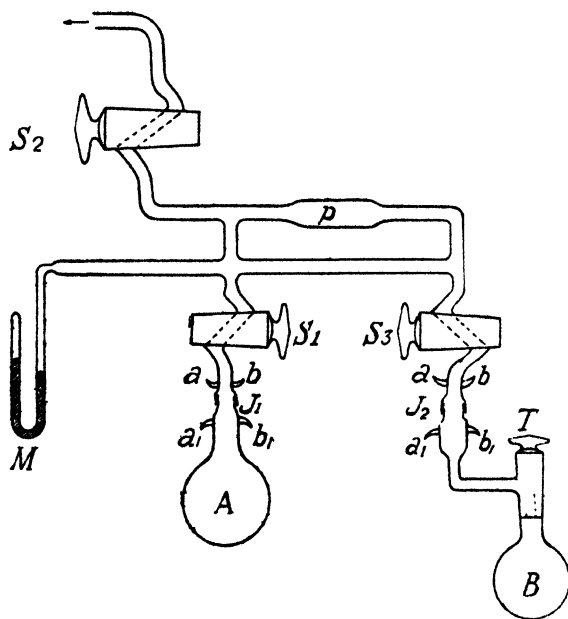


FIG. 1.

described in Part I. of this work.⁵ All the measurements were carried out in a room kept at a constant temperature of 20° C.

For the undialysed gels the vapour pressure measurements were commenced when the period of syneresis was considered to be complete. This required about 10 days. For the dialysed gel, the sample was kept immersed in distilled water—which was periodically changed—until no trace of electrolyte was obtained in the water after 48 hours' contact with the gel. In most cases this entailed a period of from 2 to 3 months.

Before placing in B, the gels were broken up into small cubes of about 2·3 mm. side. This facilitated rapid drying or wetting of the gel. The dialysed sample, after removal from the distilled water and cutting, was roughly dried with some clean filter paper.

Results.

In all the following experiments the respective samples of dialysed and undialysed gel were taken from the same specimen, thus eliminating any differences which might arise due to failure to reproduce an identical gel.

⁵ *Trans. Faraday Soc.*, 28, 1, 1932.

TABLE I.

1st Desorption.				1st Sorption.				2nd Desorption.				2nd Sorption.			
Vapour Pressure in mm. Hg.	Grm. H ₂ O per 100 gm. gel.	Mols. water per mol. silica.		Vapour Pressure in mm. Hg.	Grm. H ₂ O per 100 gm. gel.	Mols. water per mol. silica.		Vapour Pressure in mm. Hg.	Grm. H ₂ O per 100 gm. gel.	Mols. water per mol. silica.		Vapour Pressure in mm. Hg.	Grm. H ₂ O per 100 gm. gel.	Mols. water per mol. silica.	
<i>Undialysed Gels prepared with Hydrochloric Acid. Initial Silica Concentration 10.5 Per Cent. Initial Electrolyte Concentration 5.5 Per Cent.</i>															
16.10	82.3	16.2		3.69	10.9	.41		13.5	46.0	2.84		14.8	57.5	4.52	
15.75	77.1	11.2		6.26	13.7	.53		11.8	37.0	1.96		15.8	70.47	7.89	
15.3	70.8	8.1		9.00	23.6	1.00		9.6	24.0	1.06					
13.05	56.8	4.8		9.46	24.6	1.09		7.0	16.3	0.65					
12.79	50.9	3.5		9.82	26.5	1.20		6.46	14.0	0.54					
9.34	32.8	1.6		10.7	32.5	1.60		3.19	10.7	0.40					
9.10	31.1	1.5		12.3	39.5	2.18		1.00	8.95	0.34					
8.40	26.9	1.2		12.7	48.5	2.47									
7.7	26.0	1.17		13.75	48.1	3.1									
6.9	24.5	1.08		15.85	71.45	8.35									
6.06	22.1	0.95													
3.0	14.8	0.58													
2.14	12.3	0.47													
1.05	9.4	0.35													
<i>Dialysed Hydrochloric Acid Gel. Initial Silica Concentration = 10.5 Per Cent. SiO₂.</i>															
16.10	83.3	16.8		6.92	9.3	0.34		14.4	46.0	2.80					
15.8	76.26	10.5		11.30	17.6	0.72		14.25	44.8	2.70					
15.6	62.5	5.57		13.65	26.2	1.19		13.45	43.5	2.56					
12.3	32.9	1.64		14.00	28.9	1.36		13.03	42.0	2.42					
10.8	20.84	0.88		14.75	33.8	1.70		12.90	41.8	2.35					
9.2	14.6	0.57		15.70	47.6	2.98		12.35	36.9	1.96					
3.16	7.8	0.28						11.8	28.2	1.31					
0.92	5.96	0.21						10.7	19.8	0.81					
								9.4	14.2	0.55					
								4.5	8.5	0.31					
								1.5	6.7	0.24					

TABLE II.

Vapour Pressure in mm. Hg.	Grm. H ₂ O per 100 grm. gel.	Mols. water per mol. silica.	Vapour Pressure in mm. Hg.	Grm. H ₂ O per 100 grm. gel.	Mols. water per mol. silica.	Vapour Pressure in mm. Hg.	Grm. H ₂ O per 100 grm. gel.	Mols. water per mol. silica.
<i>Undialysed Gel Prepared with Sulphuric Acid. Initial Silica Concentration 10.8 Per Cent. Initial Electrolyte Concentration 6.9 Per Cent.</i>								
16.3	79.0	12.57	4.53	7.4	0.27	15.75	57.1	4.37
15.6	67.2	6.84	6.95	10.8	0.40	13.55	42.5	2.42
15.6	58.7	4.74	10.18	22.8	0.97	12.6	37.4	1.97
11.86	38.8	2.11	10.68	26.1	1.16	11.47	30.1	1.41
9.76	31.6	1.52	11.56	30.9	1.46	8.8	15.0	0.58
8.25	25.9	1.17	12.37	34.8	1.75	2.17	6.7	0.24
4.98	12.2	0.46	12.9	35.2	1.78	1.96	5.6	0.19
1.40	4.4	0.15	13.3	39.9	2.18			
			14.5	44.3	2.61			
			16.0	65.5	6.21			

Dialysed Sulphuric Acid Gel.

16.8	77.5	11.51	6.45	4.4	0.16	15.0	46.6	2.91
16.2	69.8	7.71	10.6	14.0	0.55			
14.0	44.2	2.65	12.2	23.0	1.01	12.8	37.5	2.00
12.75	35.5	1.84	13.2	33.0	1.66	12.3	31.0	1.50
11.8	26.1	1.18	13.9	36.0	1.93	11.96	25.2	1.12
10.82	18.7	0.77	16.1	47.8	3.05	10.9	17.3	0.70
7.3	8.2	0.30				9.3	10.0	0.37
3.3	3.3	0.12				2.05	1.8	0.06
1.65	1.5	0.05						

In the above gels the behaviour of the dialysed samples was the same as that observed by previous investigators, while the undialysed samples exhibited marked differences.

During the first desorption of the latter gels they spontaneously broke up into a fine powder and on bringing the gel back through the reverse cycle no appreciable change in the appearance of the gel was visible until fairly high aqueous vapour pressures were attained.

In the case of the hydrochloric acid gel, from pressures of 10 mm. upwards the gel became less opaque as its vapour pressure increased until at pressures of 12-13 mm. the material became quite transparent. As the saturation pressure of water was slowly approached, an increasing quantity of clear liquid was obtained in flask B.

A similar behaviour was observed with the acetic acid gel.

With the sulphuric acid gel, the sample swelled up into a voluminous mass at pressures between 12 mm. and 14 mm., while at higher pressures the volume contracted and a hard glassy mass was formed. Free liquid was also formed in this case as the vapour pressure approached that of pure water.

Discussion of Results.

A study of the results obtained for the undialysed gel compared with those for the same gel after the removal of the electrolyte by dialysis,

shows that the presence of a solute exerts a marked influence on the sorption of moisture by silica gels.

In the first place, for the three gels investigated, no closed hysteresis loop has been obtained, that is, in no case are the first sorption and first desorption curves connected by means of part of the second desorption curve. Such a hysteresis loop, obtained for the dialysed gels, is found in the normal type of adsorption isotherms obtained for gels. With the undialysed gels, after the first drying cycle, the sorption and desorption of water vapour appears to become completely reversible.

Secondly, consideration of the first sorption curves for any one gel in the dialysed and undialysed conditions, shows that at high water contents, a further small addition of water to the dialysed gel is accompanied by a large increase in the aqueous vapour pressure exerted, whereas with the undialysed gel a small increase in vapour pressure corresponds to a large increase in water content. In other words, in the dialysed condition at high water contents, the first sorption curve tends to become parallel to the vapour pressure axis, while in the undialysed condition the curve tends to become perpendicular to the same axis.

According to Zsigmondy's ³ theory of wetting and drying of dialysed silica gels, the vapour pressure exerted by the gel depends upon the curvature of the liquid surface inside the capillaries. During drying, the liquid is bounded by concave menisci, whose radii of curvature depend upon the diameter of the capillaries. Drying the gel is assumed to have made the walls of the capillaries less easily wetted, so that the conditions governing wetting differ from those operative during drying. With less easily wetted pore walls the menisci in the capillaries will be less concave or may even be convex. The consequence will be that, for a given water content of the gel, a higher vapour pressure will be exerted during wetting, thus giving rise to the hysteresis normally found.

Assuming the above explanation to be correct for dialysed gels, the process is, however, more complicated in the undialysed samples due to the presence of electrolyte. In this case, during the initial drying, the electrolyte will be concentrated in the gel and some capillaries may be completely filled with solute, while probably, in all cases, a layer of solid electrolyte will be deposited on the walls of the open capillaries. During the sorption, after the first desorption, the water taken up by the gel will dissolve some of the electrolyte, and in doing so will facilitate the complete wetting of the pore walls by the liquid. The result therefore will be that the layer of soluble electrolyte on the capillary walls will tend to make the wetting and drying processes, after the initial drying, completely reversible.

Taking, for example, the undialysed hydrochloric acid gel, an examination of the salt content and the total quantity of water present at various pressures showed that, at the point A (see Fig. 2) on the first desorption curve,—the water content at this point was just sufficient to dissolve all the salt present to give a saturated solution—the pressure exerted by the gel was approximately equivalent to that of the saturated solution of sodium chloride. This was not the case at the equivalent pressure (point A¹), on the sorption curve. The latter point was attained when the water content was only 80 per cent. of that at A.

The same effect is obtained with sulphuric acid gel. Here the vapour pressure of a saturated solution of sodium sulphate is attained on the sorption curve when only 65 per cent. of the necessary water, for the

complete solution of the salt, has been absorbed. Similarly for the acetic acid gel with 75 per cent. of the necessary water. Above this vapour pressure there is a steady increase of pressure with water content in both cases.

A possible explanation of this behaviour is that all the salt present in the gel is not available for solution, due probably to the tremendous contraction which takes place in the gel during desorption. This contraction amounts to about 90 per cent. of the original volume and, in the case of undialysed gels is accompanied by continual concentration and finally precipitation of salt. Part of the electrolyte in the desiccated gel may be completely enclosed and therefore inaccessible to the water in the capillaries, except by diffusion. This process would be very slow and would not influence the measurements to any great extent.

When, along the sorption curve, the point is reached where the gel exerts the normal vapour pressure of the saturated solution of the salt present, *i.e.*, point represented by A^1 in Fig. 2, the liquid surface in the gel may be bounded by minisci either of (a) zero curvature, or (b) negative

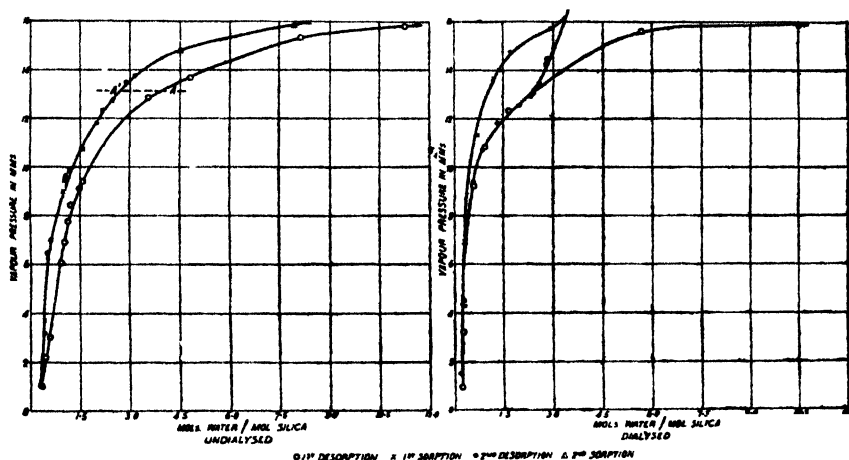


FIG. 2. HYDROCHLORIC ACID GEL.

curvature. The possibility of the surface being bounded by convex menisci is eliminated by the fact that the whole curve is reversible.

(a) Zero Curvature.—In this case the liquid surface must have reached the external surface of the gel—assuming the absence of large pores—and also be saturated with the particular salt. This means that the vapour pressure measured at any point below this value is probably that of a saturated solution under the conditions prevailing, along the liquid surface inside the gel structure, at the time of measurement.

To obtain equilibrium with still higher vapour pressures a further adsorption of water is essential, and must therefore of necessity lead to the formation of free solution. The quantity of free liquid will steadily increase with an increase in the aqueous vapour pressure with which it comes into equilibrium—the limit being reached when infinite dilution of the liquid is attained.

(b) Negative Curvature.—Since a liquid surface with negative curvature exerts a lower vapour pressure than the same liquid surface with zero curvature, it is clear that the liquid present in the gel at this point

cannot be saturated with the salt, thereby indicating that the availability of the salt for solution purposes is even less than in (a) above.

In order that the liquid surface may possess a negative curvature, it must lie inside the gel capillaries, and equilibrium with higher vapour pressures may be attained without the formation of free salt solution, as the latter will not appear until the capillaries have been completely filled.

The point at which free liquid appears is very difficult to determine experimentally, but, in the gels investigated, the presence of free liquid was observed soon after the point represented by A¹ (Fig. 2) was reached, showing that at this point the conditions discussed under (a) above were very nearly satisfied.

The general results of this investigation tend to support the conclusion that the liquid taken up along the sorption isotherm—within the limits of pressure investigated—is present in the gel in the uncombined state.

That this conclusion probably also applies to the liquid extracted during the desiccation is shown by some experiments carried out on the volume changes accompanying the initial irreversible contraction. For this purpose a series of gels of cylindrical shape and known dimensions were prepared and dialysed to remove the electrolyte. This was essential, as otherwise the crystallisation of salt would form the well-known hair-like growths over the surface of the gel. The dialysed samples were slowly desiccated at constant temperature and the contraction in linear dimensions measured by a cathetometer. By this means the changes in volume of the gel were followed until the samples had contracted to about 9 per cent. of their original volume. The average composition at this point was $\text{SiO}_2 \cdot 2\text{H}_2\text{O}$. With further desiccation the gel samples cracked and broke up spontaneously. A typical example of the values obtained is reproduced in Table IV.

TABLE IV.*

M.	T.	L.	D.	L/D.	W.	V.
	0	7.600	3.800	2.00		86.19
33.5	1	7.085	3.597	1.97	75.6298	72.01
28.1	3	6.745	3.387	1.99	64.5538	60.77
24.2	4	6.505	3.239	2.04	56.5488	53.59
21.4	5	6.130	3.124	1.97	50.7248	47.01
6.6	10	4.395	2.203	2.00	20.2942	16.75
4.8	11	3.985	2.030	1.97	16.6814	12.90
4.0	12	3.885	1.942	2.01	15.0932	11.50
3.0	15	3.590	1.807	1.98	12.9740	9.23
2.1	16	3.310	1.674	1.98	11.1136	7.29

The fluctuations observed in L/D are due to the slight distortion which takes place in the early stages due to the weakness of the gel.

The results show that the contraction was equal to the volume of liquid extracted, thus corroborating the results obtained by van Bemmelen.⁶ This means that the water must occupy the same volume

* The following abbreviations have been applied :—

T = time in days after setting. W = weight in grm.
 L = length of prism in cms. V = calculated volume in c.cs.
 D = mean (of 6) diameter in cms. M = mols. of water per mol. of silica in the gel.

⁶ van Bemmelen, *Z. anorg. allg. Chem.*, 18, 98, 1898.

in the gel as it does under normal conditions, which implies that the water present inside the gel is not in the combined state.

It should be pointed out that in the above investigation, the main object was to examine the effect of the presence of electrolyte on the vapour pressure curves for silica gels, so that the number of vapour pressure determinations carried out were not sufficient to give any information regarding the discontinuities reported by Allmand⁷ and co-workers in such vapour pressure isotherms.

Summary.

The moisture sorption isotherms of dialysed and undialysed silica gels have been determined by a static method.

The results show that after desorption, the following isotherm is completely reversible in the case of the undialysed gels, and a tentative explanation, based on Zsigmondy's theory, has been advanced.

Examination of the data obtained leads to the conclusion that the water taken up by the gel is in the uncombined state. Further evidence for this was obtained from experiments on the volume changes occurring during early desiccation.

The author would like to take this opportunity of thanking the Director of Building Research for his kind permission to publish these results. He is also indebted to Mr. B. H. Wilsdon for the untiring interest he has shown in the work.

⁷ Allmand and Burrage, *Proc. Roy. Soc.*, **130A**, 610, 1931.

*Building Research Station,
Bucknall's Lane,
Garston, Herts.*

THE TIME FACTOR IN ANODIC PASSIVATION OF METALS. REMARKS ON THE PAPER OF W. J. SHUTT AND V. J. STIRRUP.¹

BY W. J. MÜLLER (*Wien*).

Received in German on 4th February, 1932.

In their work Shutt and Stirrup measured the time of passivation by a special method with hanging gold electrodes in 2*N* hydrochloric acid and iron in 2*N* sulphuric acid at different temperatures, the electrolyte being vigorously stirred. They assume in the discussion of their results that by reason of the vigorous stirring during the experiment the formation of salt layers or surface layers (such as have been described in my earlier experiments with a shielded electrode² is excluded.

This view does not necessarily follow when consideration is given to our earlier experimental results. In my lecture on "the Passivity of Metals" a diagram is given which shows that the relationship

¹ W. J. Shutt and V. J. Stirrup, *Trans. Far. Soc.*, **26**, 635, 1930.

² W. J. Müller, "On the Passivity of Metals," *Trans. Far. Soc.*, **27**, 736, 1931, where the earlier work is also discussed.

$\log t_p = \log B - n \log i_0/F_0$ or $t_p = B(i_0/F_0)^{-n}$, involving the factor $i_0 t_p$, deduced from the layer theory, holds good up to current densities of over 3 amps. per cm.² and passivating periods of some one-tenth of a second. The difference between the behaviour of a shielded electrode and that of a hanging electrode exposed to diffusion or an electrode in a stirred electrolyte is set forth in the work with Löwy and is mentioned on page 744 of my lecture. Since the surface layer proves to be very thin at high-current densities, its formation takes place at high-current densities in the diffusion layer of the electrolyte lying on the metal; as has been shown by Nernst and his school, this is not affected by the motion in the vigorously stirred electrolyte. We should therefore expect that at very high-current densities the difference between the time of passivation of a shielded and of a stirred electrode would be practically negligible whilst at lower-current densities it would be very

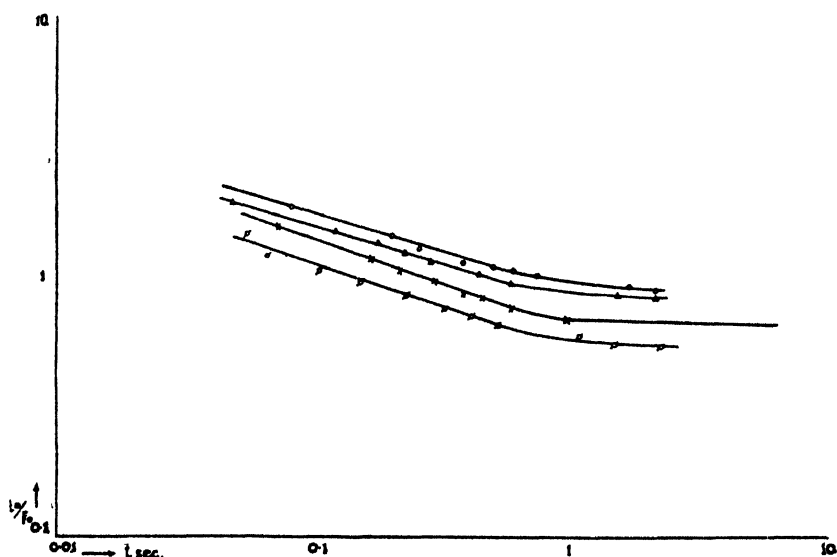


FIG. 1.

Shutt and Stirrup: Au in 2N HCl.

○ 29.5° C.

△ 20.0° C.

× 9.5° C.

φ 1° C.

large, as is indeed shown by the diagram on page 744 in which are shown the figures for a stirred electrolyte at about 1 amp./cm.² It was to be expected, therefore, that the experimental results of Shutt and Stirrup when plotted on a double logarithmic scale would give at current densities over 1 amp. a straight line for the $i_0 t_p$ relationship which, below about 1 amp., would deviate from the straight for longer times of passivation. In Fig. 1 the experimental results of Stirrup for different times of passivation and temperatures have been plotted in this way for gold. We see that at higher-current densities the linear relationship is well fulfilled, and that at lower-current densities the curve bends away for longer times of passivation in a similar way to the curve on page 744. Moreover, the displacement with temperature is quite in accord with the surface layer theory; at lower temperatures the times of passivation, corresponding to the lower solubility of the salts forming the surface layer, are noticeably smaller.

According to the surface layer theory a porous film is built up by chemical passivation the thickness of which under equilibrium conditions is independent of the original passivating current density, because under those conditions layer formation and solution are in equilibrium. From this it follows that the time for the solution of this layer which corresponds to the "time of recovery" of Shutt and Stirrup, must be independent of the original passivating current density. On the other hand, the time of recovery must be related to the solubility of the layer in the electrolyte, quite independently of whether the layer is dissolved by a simple solution reaction or whether it goes eventually into solution by the agency of a local current; it must therefore be longer at lower temperatures, as indeed was found by Shutt and Stirrup.

Fig. 2 shows the results of Stirrup for iron plotted on a double logarithmic scale, and they indicate the validity of the $i_0 t_p$ ratio in this case. On the curve of Shutt and Stirrup at 20° there are shown the values of

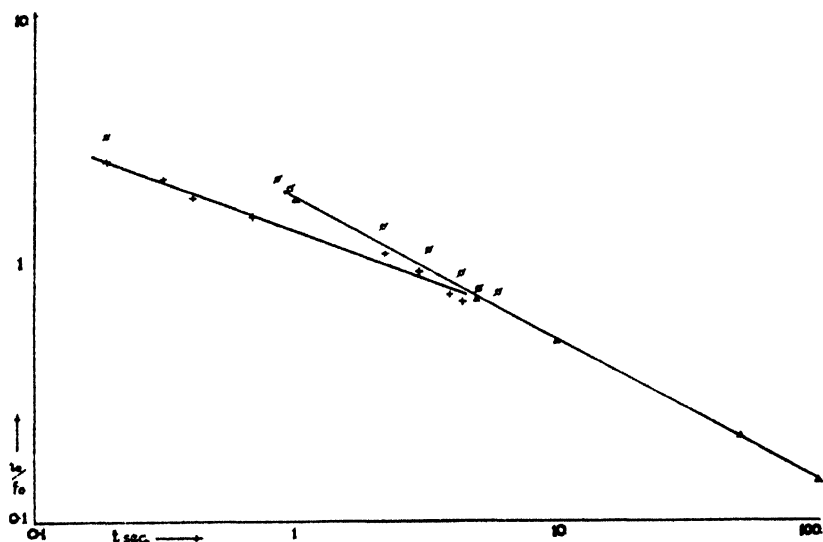


FIG. 2.

Shutt and Stirrup: ϕ + Fe in 2N H_2SO_4 .

Müller and Löwy: Δ " " "

$\phi \Delta$ Temp. 20° C. + Temp. 6° C.

$i_0 t_p$ in 2N sulphuric acid obtained by ourselves with Löwy. We see that at lower-current densities the figures of Shutt and Stirrup lie, as was to be expected, below the curve for the shielded electrode, but that at higher-current densities they lie practically on the curve. The values at 6° of Shutt and Stirrup at high-current densities correspond to shorter times of passivation. The direction of the curve shows clearly, however, that at lower-current densities the time of passivation is extended as one might expect in the case of a stirred electrode. Moreover, the times of recovery of the passivated electrode correspond with those we should expect in accordance with the layer theory, in much the same way as has been explained in the case of gold.

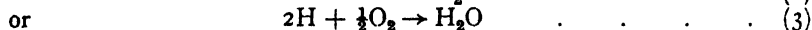
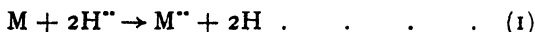
*Institut für Chem. Technologie
Anorgan. Stoffe der Technischen Hochschule,
Wien.*

A METHOD FOR THE MEASUREMENT OF THE DISSOLUTION OF METALS IN SALT SOLUTIONS.

By L. WHITBY.

Received 4th February, 1932.

The dissolution of metals in aqueous solutions may be represented as follows :—



Some H_2O_2 may also be formed.

The progress of attack may be measured, therefore, by following the course of both hydrogen evolution and oxygen absorption. Bengough, Stuart, and Lee,¹ have developed a method, capable of yielding accurate periodic measurements of the progress of the reaction, which depends on determinations of the volume changes which occur in a closed vessel under constant pressure, before and after removal of hydrogen by combustion. This method is not suitable when the hydrogen evolution rate is high, consequently a new procedure has been adopted for such reactions as that of magnesium in chloride solutions, etc.

The method consists of the periodic withdrawal from the corrosion vessel of samples of the gas above the corroding liquid, which are then subjected to determinations of their hydrogen and oxygen contents.

Let the volume of air in the corrosion vessel before commencement of the reaction be V c.c. containing a c.c. of oxygen.² At the time of withdrawal of the sample assume that corrosion has resulted in absorption of a' c.c. of oxygen and evolution of b c.c. of hydrogen, then the total volume of gas in the vessel will be :

$$V - a' + b \text{ c.c.}$$

If a sample V' c.c. of the gas is then found to contain v_0 c.c. of oxygen and v_H c.c. of hydrogen, the volume of oxygen in the vessel at the time of withdrawal of the sample would have been :

$$\frac{v_0}{V'}(V - a' + b) = a - a' \quad . \quad . \quad . \quad (1)$$

Similarly the volume of hydrogen would have been :

$$\frac{v_H}{V'}(V - a' + b) = b \quad . \quad . \quad . \quad (2)$$

Whence :

$$b = \frac{v_H(V - a)}{V' - v_0 - v_H} \quad . \quad . \quad . \quad (3)$$

and

$$a' = a - \frac{v_0(V - a)}{V' - v_0 - v_H} \quad . \quad . \quad . \quad (4)$$

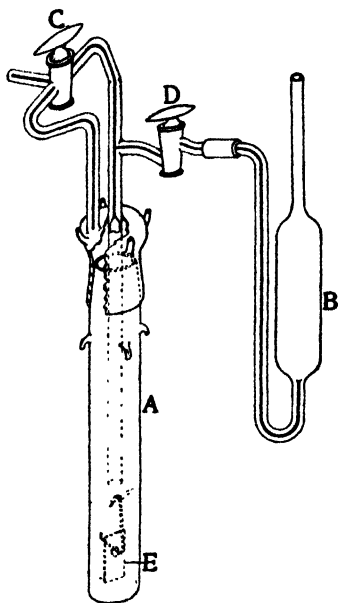
¹ *Proc. Roy. Soc.*, 116A, 425, 1927; 121, 88, 1928.

² All gas volumes are assumed to be at N.T.P.

Experimental.

Details of a typical corrosion vessel approximately 200 c.c. internal volume are shown in the figure (A). After suspending, by means of a thin glass hook, a suitable specimen (E) of the metal under investigation, the cap, lubricated with a mixture of vaseline and paraffin wax, is replaced and sealed with vacuum wax; it is then wired down, utilising the glass hooks illustrated, and the vessel clamped rigidly in a water thermostat, being immersed to a point just below the bottom of the taps. A stream of purified air is then passed through the vessel and tap D closed. Fifty c.c. of the desired corroding liquid are then pipetted into the vessel B and the whole system left for about 3 hours to reach thermal equilibrium. Tap D is then opened and tap C so adjusted that by connecting a source of purified compressed air to the top of B, the liquid may be driven over into A. The air used for this purpose is filtered and passed through potash solution, after which it bubbles through 3 Babo's towers filled with distilled water and immersed in the thermostat, finally passing through a Jena glass filter before reaching B. Before closing the taps of the corrosion vessel the barometric pressure is noted.

A compensated Hempel gas-burette, calibrated to convert gas readings to N.T.P., and with mercury as the confining liquid, is periodically connected to tap C, which may be so adjusted that the gas sample is withdrawn from both top and bottom of the vessel. Thorough mixing of the gas may be performed, however, by lowering and raising the levelling bulb of the burette several times, thus alternately withdrawing and driving back the gas. After removal of the sample, the gas remaining in the vessel is swept out and replaced by purified air and the barometric pressure again noted.



Hydrogen in the gas sample is determined by passing the gas over palladium-black, the remaining oxygen then being determined by phosphorus; a complete determination may be performed in about twenty minutes.

The application of equations (3) and (4) necessitates a knowledge of the oxygen content of the purified air used, together with the volume of the gas space of the corrosion vessel, and the tension of aqueous vapour therein.

The oxygen content of the purified air should be determined in a sample that has reached the temperature of the thermostat.

The gas volume of the corrosion vessel is difficult to determine directly; an indirect method utilising the change in pressure that occurs when a known volume of gas is withdrawn has been adopted. The measuring instrument is an adapted compensated Hempel burette; details are given elsewhere.³

³ Whitby, *J. Sci. Instr.*, 8, 117, 1931.

The tension of aqueous vapour in the corrosion vessel has been taken as that due to saturated water vapour at the same temperature; so far only dilute solutions have been investigated so that the assumption is no doubt justified. It can be shown, however, that large errors in this figure have no appreciable effect on the results.

Application to Magnesium.—The method has been applied to the dissolution of magnesium in dilute sodium chloride solutions. It has been assumed by previous authors that there is a complete lack of oxygen absorption during the dissolution of magnesium in chloride solutions,⁴ but no direct experimental proof has been advanced in the case of very dilute solutions where it is difficult to take the reaction to completion.

Confirmation of the lack of oxygen absorption resulting from the dissolution of magnesium in $N/10,000$ and $N/1,000$ sodium chloride solutions has now been obtained. The metal used was foil, 0.2 mm. thick and containing 99.95 per cent. magnesium. The specimens were 1.5 cm. by 4 cm. in size and were suspended with a thin glass hook through a punched hole 0.6 cm. diameter. The solutions were made from Kahlbaum sodium chloride and laboratory distilled water, redistilled from alkaline potassium permanganate.

In the case of $N/10,000$ sodium chloride solution the total hydrogen evolution at the end of 108 days was 2.22 c.c. and 1.45 c.c. respectively, from duplicate specimens. These figures are the sum of 11 separate determinations in which the oxygen absorptions varied from +0.1 c.c. to -0.2 c.c., a slight negative absorption usually occurring. Since the figures are cumulative, a negative absorption of some 0.5 c.c. of oxygen had apparently occurred at the end of 108 days. The figures for $N/1000$ sodium chloride solution were similar for the apparent oxygen absorption, although in this case the total hydrogen evolution at the end of 63 days was over 40 c.c. It is shown later that the maximum error in the determined oxygen absorption due to reading errors of the burette may amount to nearly ± 0.2 c.c., therefore an apparent oxygen absorption of 0.1 c.c. in any one determination may be neglected. Actually, however, a consistent negative absorption appeared to occur, and it is suggested that the purified air used had not quite reached the temperature of the thermostat (25°) before passing into the corrosion vessel, thus causing an apparent slight excess of oxygen over the theoretical amount. In cases where high accuracy is required, the use is suggested of a long glass grid in the thermostat to pass the air through before reaching the vessel.

The figures, however, leave no doubt of absence of oxygen absorption in the dilute solutions investigated, and in the light of these results it does not seem likely that oxygen absorption occurs in more concentrated solutions, where the rate of hydrogen evolution is higher.

Precision of Measurements.

A study has been made of the most probable maximum deviations from the true values of oxygen absorption and hydrogen evolution, due to errors in reading the burette.

⁴ Lemoine, *Compt. rend.*, **129**, 291, 1899; Tommasi, *Bull. Soc. Chim.*, (3), **21**, 885, 1899; Kahlenberg, *J. Amer. Chem. Soc.*, **25**, 380, 1903; Roberts and Brown, *ibid.*, **25**, 801, 1903; Getman, *ibid.*, **38**, 2594, 1916; **39**, 596, 1917; Hughes, *J. Chem. Soc.*, **115**, 272, 1919; Portevin and Pretet, *Rev. Met.*, **26**, 259, 1929; Bekier and Zablocki, *Rocz. Chem.*, **10**, 314, 1930.

Starting from equation (3) above. Then

$${}_b\Delta_{v_H} = \pm \frac{\partial b}{\partial v_H} \delta_H \quad . \quad . \quad . \quad . \quad (5)$$

where ${}_b\Delta_{v_H}$ is the deviation from the true amount of hydrogen evolution due only to the small error δ_H in reading the contraction due to absorption of hydrogen in the analysis.

Values are assigned to the terms involved as follows: The free gas space, V , of a 200 c.c. corrosion vessel is 150 c.c., from which with a 100 c.c. burette, a gas sample, V' , of 65 c.c. may be withdrawn. If corrosion results in only a small change in the composition of the air in the vessel, then $V - a = 120$ c.c., $V' - v_0 - v_H = 52$ c.c., and $v_0 = 13$ c.c. For v_H the small value of 1 c.c. may be chosen, since larger values would result in a smaller percentage deviation.

The reading error δ_H may be placed equal to ± 0.05 c.c. when dealing with a burette graduated to 0.2 c.c.

Partial differentiation of b in equation (3) with respect to each of the terms v_H , V , a , V' and v_0 respectively, and substitution of the values assigned to the terms as above, results in the following individual deviations:—

$$\begin{aligned} {}_b\Delta_{v_H} &= \pm 0.1 \text{ c.c.} \\ {}_b\Delta_V &= \pm 0.001 \text{ c.c.}^5 \\ {}_b\Delta_a &= \pm 0.001 \text{ c.c.} \\ {}_b\Delta_{V'} &= \pm 0.002 \text{ c.c.} \\ {}_b\Delta_{v_0} &= \pm 0.002 \text{ c.c.} \end{aligned}$$

The most probable total maximum deviation due to these individual deviations is given by the square root of the sum of their squares, hence

$$\Delta b = \pm 0.1 \text{ c.c.}$$

Proceeding in a similar way in equation (4),

$$\begin{aligned} {}_a'\Delta_{v_0} &= \pm 0.14 \text{ c.c.} \\ {}_a'\Delta_a &= \pm 0.06 \text{ c.c.} \\ {}_a'\Delta_V &= \pm 0.13 \text{ c.c.} \\ {}_a'\Delta_{V'} &= \pm 0.03 \text{ c.c.} \\ {}_a'\Delta_{v_H} &= \pm 0.03 \text{ c.c.} \end{aligned}$$

whence

$$\Delta a' = \pm 0.2 \text{ c.c.}$$

If equations (3) and (4) are put in the form

$$b = \frac{0.8Vv_H(p_a - p_{H_2O})}{760(1 + \alpha t)(V' - v_0 - v_H)} \quad . \quad . \quad . \quad (6)$$

and

$$a' = \frac{V(p_a - p_{H_2O})[0.2(V' - v_0 - v_H) - 0.8v_0]}{760(1 + \alpha t)(V' - v_0 - v_H)} \quad . \quad . \quad (7)$$

respectively, where p_a is the initial pressure, in millimetres of mercury, of the atmosphere in the vessel, and p_{H_2O} is the pressure of aqueous vapour in the vessel, then the effects of deviations from the true value of p_{H_2O} are found by partial differentiation of b and a' respectively with respect to p_{H_2O} . The relative numerical magnitudes of $\partial b / \partial p_{H_2O}$ and

⁵ δ_V for a 200 c.c. vessel is taken as ± 0.54 c.c. (Whitby, *loc. cit.*).

$\partial a' / \partial p_{H_2O}$ obtained in this way are of negligible order, indicating that large errors in the value of the tension of aqueous vapour in the vessel may be neglected.

Further important facts are that the greatest error in the determination of the hydrogen evolution is likely to arise from faulty determinations of hydrogen in the sample; the actual deviation due to this cause,

Zn Used. Mgms.	Total Hydrogen Evolved, c.c. N.T.P.	
	Theor.	Found.
4.5	1.5	1.5
6.2	2.1	2.1
19.2	6.5	6.3
22.4	7.6	7.5
49.6	16.9	17.0
53.0	18.0	17.7

however, remains fairly constant over an extended range of hydrogen concentration, negligible errors only are caused by normal reading errors in the other terms of equation (3).

The greatest error in the determination of oxygen absorption is likely to arise from errors in the values of the volume of the corrosion vessel, the volume of oxygen in the sample of gas taken, and, to a lesser extent, from errors in the previously determined original oxygen content of the gas. It must be emphasised that since the errors discussed are the maximum probable errors, they will rarely be realised.

The validity of equation (3), above, was confirmed by determinations of hydrogen evolved from small quantities of zinc dissolved in dilute sulphuric acid in the corrosion vessel. Results are tabulated below, agreement between the theoretical and experimental results is good, and part of the small differences are no doubt due to hydrogen solubility.

Summary.

A simple method for following the dissolution of metals in salt solutions is based on determinations of the volumes of oxygen absorbed and of hydrogen evolved by analysis of samples of gas periodically removed from above the corroding liquid.

Application of the method to the dissolution of magnesium in $N/10,000$ and $N/1000$ sodium chloride solution has confirmed the absence of appreciable oxygen absorption in these cases.

The precision of the measurements has been investigated and checked by determinations of the hydrogen evolved from small quantities of zinc, and has indicated that serious deviations from the true values are not probable.

The author is indebted to Dr. G. D. Bengough for helpful advice and interest. The work has been carried out for the Corrosion of Metals Research Committee of the Department of Scientific and Industrial Research, and the thanks of the author are due to the Chairman, Professor Sir Harold Carpenter, F.R.S., and to Professor G. T. Morgan, F.R.S., Director of Chemical Research, for facilities afforded and for permission to publish.

*Chemical Research Laboratory,
Teddington, Middlesex.*

ELECTRIC DISCHARGES IN LIQUIDS. PART I— THE ARC DISCHARGE IN WATER.

By HERBERT DYSON CARTER AND ALAN NEWTON CAMPBELL.

Received 8th February, 1932.

Davy¹ was the first to observe that the electric arc would continue to "burn" when immersed in water, and Masson² fifty years later made observations on the spectra of such arcs. The decomposition of water vapour by electric spark discharges was noted and briefly studied by Perrot,³ whose work was expanded by Buff and Hofmann.⁴ At the same time the spectra of such discharges received attention from Liveing and Dewar,⁵ Konen,⁶ and others. Lepsius⁷ had employed carbon electrodes in an arc burning under water, but his work was repeated and extended by Löb,⁸ with considerably different results: both workers studied the gaseous reaction products to some extent qualitatively, and Löb concluded that the reaction was a purely "pyrogenetic" one, analogous to that taking place when hot wires are plunged into liquids. Organic liquids as well as water were employed, but the solid products received little attention.

At this time Bredig⁹ commenced his work on the production of colloids by arcing metals in liquids, and Svedberg¹⁰ noted a difference in the products of direct and alternating current arcs, and modified the Poulsen rectifier by burning the arc in organic liquids.¹¹ Chapman and Lidbury,¹² Holt and Hopkinson,¹³ and J. J. Thomson,¹⁴ working mostly with spark discharges in water vapour, observed a wide divergence from Faraday's law, but failed to provide a suitable hypothesis for the reaction. The work of Kernbaum¹⁵ and Makowetzky¹⁶ has shown that the products are more complex than at first believed, and that they vary greatly with the type of discharge and electrodes employed: theories of the reactions were also advanced. Müller¹⁷ studied the spark discharge in liquid air, showing how completely the reactions differed from those taking place in the ordinary air spark; he also observed a solid product not colloidal in character. Recently Shipley

¹ Davy, *J. Roy. Inst.*, **1**, 165, 1802.

² Masson, *Ann. Chim. Physique*, **31**, 295, 1851.

³ Perrot, referred to by J. W. Mellor, *Comprehensive Treatise on Inorganic Chemistry*, Vol. I, p. 493, 1922.

⁴ Buff and Hofmann, *Ann. Chim.*, **113**, 129, 1860.

⁵ Liveing and Dewar, "Collected Papers on Spectroscopy," Cambridge University Press, 1915; papers in *Proc. Roy. Soc.*, 1880 *et seq.*

⁶ Konen, *Ann. Physik*, **4**, 742, 1902.

⁷ Lepsius, *Ber.*, **23**, 1418, 1637 and 1642, 1890.

⁸ Löb, *Ber.*, **34**, 915, 1901. ⁹ Bredig, *Z. Elektrochem.*, **4**, 514, 1898.

¹⁰ Svedberg, summarised in the text *Formation of Colloids*, 1921.

¹¹ Svedberg, *Physik. Z.*, **15**, 361, 1906.

¹² Chapman and Lidbury, *J. Chem. Soc.*, **81**, 1301, 1902.

¹³ Holt and Hopkinson, *Phil. Mag.*, **16**, 92, 1908.

¹⁴ Thomson, J. J., *Recent Advances in Electricity and Magnetism*, p. 181, 1892.

¹⁵ Kernbaum, *Compt. Rend.*, **151**, 319, 1910 (and other papers in this journal).

¹⁶ Makowetzky, *Z. Elektrochem.*, **17**, 217, 1911.

¹⁷ Müller, *Z. anorg. Chem.*, **76**, 324, 1912.

and Goodeve¹⁸ investigated high voltage arcs in alkaline electrolytes with various electrode materials, but all of the products were not studied. Many papers, notably those by Tarczynski,¹⁹ and Fowler and Mardles,²⁰ have been published dealing with discharges in organic liquids, but it may be said that the existing knowledge of these reactions is still incomplete. In no cases have the relationships between the electrical energy input and the heat energy developed been studied.

The Nature of the Problem.

The work to be outlined below was done with two general objects in view :

1. To determine qualitatively and quantitatively the complete products of the various discharges, and
2. To determine, if possible, the mechanism of the reactions taking place.

In all cases it was recognised that not only do the electrodes and liquids employed affect the reactions, but that the nature of the discharge must be carefully controlled if the results obtained are to be comparative, a fact not always realised by earlier workers. In this part only the low tension arc discharge in liquid water is covered, carbon electrodes being employed in most of the experimental work and metal electrodes only occasionally.

1. Characteristics of the Arc Discharge.

The essential feature of the arc discharge in gases is the production of heat, light, and chemical change, and in this respect the arc burning in liquids differs but little. To the eye, however, the two types of discharge are quite dissimilar; the characteristics of low voltage arcs in water and organic liquids have been incompletely described by Konen,⁶ and those of spark discharges by Tian,²¹ Henri,²² Howe,²³ and others. Shipley and Goodeve¹⁸ studied fully the appearance and certain electrical effects of high voltage A.C. arcs in electrolytes.

The arcs discussed below have several very characteristic features. They are produced by *striking*, a method mentioned in only a few of the papers referred to above; that is, the electrodes are brought together while connected to the source of current, and then separated slightly. With low voltages (from 6 to 50 volts A.C. or D.C.) the arc is extremely short, and may best be maintained with the electrodes in actual contact, a distinguishing feature. It appears as a brilliant spot emitting a very intense light, the region of arcing occurring not at the point of contact, and shifting continually as the electrode material is worn away. A sound of variable frequency is produced and the emitted light is rich in ultra-violet radiations, as many workers have noted, *e.g.* Howe.²³ At all times during arcing a stream of gas bubbles, giving off a distinct odour, rises from the incandescent region, violently agitating the liquid, and when the water is kept near the boiling-point large amounts of steam also are evolved. The heat developed makes cooling necessary,

¹⁸ Shipley and Goodeve, *Eng. Jour. Can.*, 10, 3, 1927. Also Shipley, *Can. Jour. Res.*, 1, 305, 1929.

¹⁹ Tarczynski, *Z. Elektrochem.*, 22, 252, 1926.

²⁰ Fowler and Mardles, *Trans. Far. Soc.*, 23, 301, 1927.

²¹ Tian, *Compt. Rend.*, 1483, 1911.

²² Henri, *Physik. Z.*, 14, 516, 1913.

²³ Howe, *Physic. Rev.*, 8, 674, 1916.

either by circulation or by supplying fresh water to the arc. The liquid rapidly becomes cloudy with particles from the electrodes, most of which are not colloidal.

A most important feature is that these arcs can be maintained only in water of low conductivity (distilled or good tap water). The addition of small amounts of electrolyte prevents the production of, and immediately inhibits any existing, arcing; the arcing being replaced by extensive electrolysis. When arcing occurs a strong electric field, which may be detected by the fingers, exists in the surrounding liquid, similar to that observed by Pfanhauser²⁴ during electro-plating under special conditions.

These characteristics make it impossible to secure an arc which is automatic in adjustment, since the electrodes must be continuously moved in a manner only developed by experience. If a mechanical vibrator be substituted for hand adjustment then the arc is frequently *broken* and when this occurs electrolysis takes place, giving products not associated with the true arc reactions. For low voltage work hand manipulation of at least one electrode is therefore necessary, and the lower the voltage employed the more frequent is the adjustment required. With metal electrodes "welding" is almost continuous unless over 50 volts be applied, when the ends may be separated slightly.

2. Apparatus.

Direct current from a 120-volt main was the source of power in all experiments, this being passed through two heavy line resistances. This precaution was necessary since the resistance of the arc is almost zero at the time of striking, but rises to about 2 ohms during arcing. By varying the line resistance the voltage across the arc may be altered, but this factor also depends upon the back E.M.F. of the arc, which is considerable. Generally the voltage across the arc fluctuates widely and with great rapidity while the current is relatively steady. Neither of these factors can be read precisely upon meters of ordinary construction, and only a rough eye approximation can be obtained. An apparatus for measuring accurately the mean amperage and voltage supplied to the arc has been constructed, and the results obtained with it will be reported later.

The arc was operated in a small copper chamber fitted with a window of thin sheet mica for observation. The electrodes were horizontally opposed and entered the chamber through lubricated rubber sleeves. Outlets were provided for the removal of the gaseous products and the liquid remaining after arcing; the former was shielded by a baffle which prevented the escape of the liquid, but allowed free circulation of gases. The whole chamber was immersed in a metal calorimeter vessel of one litre capacity, the electrodes being admitted through seals similar to the above. This outer container was filled with water circulated by a stirrer, and served to keep the liquid in the inner arc chamber below 30° C. during a run; it was also employed as a calorimeter in measuring the thermal energy output of the arc.

To prevent water vapour or spray entering the gas absorption train a glass wool tube immersed in a freezing mixture was connected to the chamber outlet, and followed by a sulphuric acid tube. Carbon dioxide was removed by a train of KOH bulbs and soda-lime tubes, and the

²⁴ Pfanhauser, *Z. Elektrochem.*, 7, 895, 1901.

residual gas was collected over water containing baryta. The volume of the gas was determined by displacement of water, and was measured at atmospheric pressure.

Certain experiments were facilitated by operating the arc outside of this apparatus in a small Pyrex beaker; any such modifications employed are given in their proper sections.

3. The Gaseous Products of the Discharge.

Several types of carbon electrodes were employed, but after analysis a hard uncured "projector" carbon was selected for this work; it contained 96 per cent. carbon, the impurities being silica (2 per cent.), iron (1.4 per cent.), alumina (0.6 per cent.) and traces of lime. As oxides these substances have little effect upon the reaction products, as will be seen later.

The water used in the runs was distilled and air- and carbon dioxide-free. After each run the liquid remaining was titrated for carbon dioxide, using excess baryta and succinic acid, but the correction was very small; the train was found to absorb all but traces of this gas. The air in the apparatus was either estimated and a correction applied, or the train was filled with the gas before weighing.

About one litre of gas, from which the carbon dioxide has been absorbed, collects during a five to ten-minute run, the amount depending upon many factors. The analyses were done in a Burrell apparatus, fully described in a U.S.A. Bureau of Mines Bulletin ²⁵; carbon monoxide and hydrogen were estimated by the copper oxide method with electrical heating, and saturated hydrocarbons in a combustion pipette. The cuprous chloride method for carbon monoxide was found to be quite unreliable, in accordance with the results of many workers.

While the analyses of any one gas sample gave results checking to 0.2 per cent., successive gas samples showed a wide variation, as will be seen in Table I. The copper oxide was held at 290° C. to 310° C. which was apparently high enough to burn all carbon monoxide and hydrogen; the "residue" is to a great extent nitrogen from the contained air, and the gas percentages were not corrected for this, for reasons given later.

TABLE I.

CO ₂ Per Cent.	CO. Per Cent.	O ₂ Per Cent.	H ₂ Per Cent.	Saturated Hydrocarbons. Per Cent.	Gaseous Residue. Per Cent.
9.9	16.6	1.7	53.4	6.1	12.4
9.8	17.0	3.1	47.0	Traces.	16.3
11.5	18.1	3.8	44.4	5.3	16.9
8.1	20.9	4.6	52.3	1.4	12.7

The carbon monoxide and hydrogen contents differ widely from those obtained by Löb,⁸ whose results differed from those of Lepsius,⁷ although similar methods of analysis were employed by these workers. Modern work would certainly point to the copper oxide method being the more accurate, and the use of cuprous chloride solutions for CO would perhaps

²⁵ Burrell, Siebert and Jones, *U.S. Dept. of Commerce, Bureau of Mines, Bulletin No. 197*, p. 40, 1926.

explain these differences. Löb⁸ gives percentages of CO₂, CO and H₂ which add up to 99.8 per cent., and this throws suspicion upon his results. With water and carbon electrodes considerable quantities of nitrogen and oxygen are almost certain to be in the collected gas, unless special precautions are taken, and a non-combustible gaseous residue has always been observed by us.

While the gas percentages have not yet been correlated with the factors affecting the arc operation, it seems apparent that the percentage composition depends upon these factors as well as upon the nature of the electrodes. In no case were any unsaturated hydrocarbons observed with fuming sulphuric acid or saturated bromine water as the absorbent; the amount of saturated hydrocarbons varied from mere traces to 6 per cent. The smell would indicate the presence of traces of unsaturated hydrocarbons, though not observed in the analyses.

The question of free oxygen being produced in the arc is of importance theoretically, and special tests were made to clear this up. Estimation of the air content of the apparatus is subject to error, and therefore runs were made in which the gas was collected by displacement of water from a cylinder held directly over the arc. During the run the water, previously distilled and boiled, was kept boiling vigorously in a pyrex vessel to prevent any dissolving of air. The electrodes were heated white hot in air, and then boiled in distilled water before each run; this treatment was found by Konen⁶ to be sufficient to remove air from such carbon rods. The gas produced was led directly through water-filled tubing into the burette of the gas analysis apparatus. Absorption with fresh alkaline pyrogallol solution showed only traces of oxygen, less than the limit of accuracy of the apparatus (0.2 per cent.), when care was taken to keep the arc in operation during the entire run. Since it is virtually impossible to prevent the arc breaking for a second or so during a long run, the electrolysis which occurs during these periods probably explains the presence of oxygen in the gas mixture, and it may be said that no free oxygen is produced by the arcing itself. The oxygen percentages in Table I. are corrected for a large part of the air present in the apparatus, and are no doubt the result of electrolysis.

Gaseous Residue.—In every case there remained in the analysis burette a 5 to 6 per cent. non-combustible gas residue, not accounted for by the nitrogen in the contained air. When a run was made for free oxygen, as above, and the CO and H₂ and hydrocarbons removed, this residue was reduced to 4 per cent.; since no air had been introduced into the apparatus it could not be assumed that the gas was nitrogen. A special apparatus was constructed to remove all gases except nitrogen, and the residue was transferred to a pyrex tube containing calcium chips; on heating to yellow heat, the gas was entirely absorbed. The ammonia test for calcium nitride could not be applied because of the small amount of gas (5 c.c. from a 1000 c.c. sample), and at the temperature employed the calcium would have absorbed many gases, including hydrogen.

A sample of the gaseous residue was dried over P₂O₅ and passed into a Geissler tube. Examination in the spectrometer revealed an intense hydrogen spectrum, several lines of the secondary spectrum being observed; the tube was tested with dried air, and shown to contain no water vapour or hydrogen. It is evident, therefore, that there was at least a trace of hydrogen in the residual gas, this having resisted oxidation by the copper oxide. The major portion of the gas was

undoubtedly nitrogen, although Konen⁶ found his treatment, as employed here, sufficient to remove even spectroscopic traces of nitrogen from carbon rods; considering the absorbing powers of carbon this hardly seems likely.

A similar nitrogen residue was obtained with hard carbon and with soft graphite rods.

Kernbaum¹⁵ found only hydrogen produced when water was decomposed by the action of light, radium and electric discharges, assuming that hydrogen peroxide accounted for the oxygen. In some papers dealing with the decomposition of water by several methods there has been mentioned an absence of stoichiometrical relations in the quantity of hydrogen and oxygen produced. Linder²⁶ observed this with the glow discharge in water vapour, and could not trace the oxygen to hydrogen peroxide or ozone. Urey and Lavin²⁷ failed to find any error in similar results with a discharge tube, and Bates and Taylor²⁸ reported the same thing in the photochemical decomposition of water. In many cases a gas remaining after analysis was assumed to be nitrogen.

Attempts to find a "mass balance" in the amounts of hydrogen and oxygen produced in the arc gave no conclusive results, the discrepancies being far beyond the limit of error of the methods employed. In most cases there was about 25 per cent. (by weight) excess of hydrogen over the theoretical amount corresponding to the total oxygen, free and in combination; this pointed to the existence of products other than the gases already discussed.

4. Solid Products of the Discharge.

(a) **Carbon Electrodes.**—Practically every paper on arcs under liquids mentions the formation of "cloudy dispersions" or "muddy" liquids during the operation of the arc, whether carbon or metallic electrodes were used. Before the work of Bredig⁹ such effects were not further studied, but in later papers the dispersions were dismissed as being purely colloidal suspensions of the electrode material.

When carbon electrode arcs with about 15 amperes at 30 volts D.C. have been operated in pure water for a considerable time (15 minutes in 300 c.c. of water, externally cooled) the water becomes dense black, and if allowed to stand for half-an-hour a very characteristic substance settles out. It is very flocculent and light, closely resembling metallic hydroxides in character except that it usually has only the faintest tinge of green or yellow colour. Under the microscope this substance is quite distinctive, although granules of solid carbon may be seen mixed with it. It takes the form of almost transparent plates and "strings," joined together in long chains; the plates are tinged green by transmitted light.

By carefully shaking a freshly produced dispersion of this sort the flocculent substance was obtained almost free of carbon particles, the latter sinking to the bottom relatively easily. The light substance could then be filtered off and dried.

Combustions of this substance were made in the same apparatus used for analysing the electrodes, in which the sample could be heated to a white heat while visually observed. Observation was required,

²⁶ Linder, *Physic. Rev.*, **38**, 679, 1931.

²⁷ Urey and Lavin, *J. Am. Chem. Soc.*, **51**, 3290, 1929.

²⁸ Bates and Taylor, *J. Am. Chem. Soc.*, **49**, 2438, 1927.

since the heat source had to be removed once the combustion started, otherwise it proceeded rapidly with a small explosion in some cases, and thus collection of all the carbon dioxide produced was impossible. Bright white heat was necessary completely to burn the substance in oxygen.

The samples were air-dried and then desiccated over sulphuric acid at atmospheric pressure for forty-eight hours. On heating to red heat a partial combustion took place, the loss in weight being 24 to 25 per cent.; very little carbon dioxide and some water was produced. Complete combustion gave the substance a percentage composition as follows: 2 to 3 per cent. hydrogen; 65 to 70 per cent. carbon, and 25 to 30 per cent. oxygen. The variations in the results were no doubt due to the varying amount of solid carbon contained in the substance, it being impossible to eliminate this entirely. The composition was practically the same whether the hard or soft carbon electrodes were used in the preparation of the sample, and extended drying had no effect.

It appears that this substance is similar in nature to the so-called "graphitic acid" or oxide. While this has been shown to be not a true compound, combustions give formulæ such as $C_{11}H_4O_5$ and $C_{11}H_4O_7$; Mellor,²⁹ and Hulett and Nelson^{29a} give a summary of the work on this substance. At red heat graphitic acid changes to a soft black substance ("pyrographitic" acid: $C_{22}H_2O_4$), the change representing a loss in weight of 23 per cent. approximately. This agrees well with the results given above, and since graphitic acid is roughly 2 per cent. hydrogen, 63 per cent. carbon, and 35 per cent. oxygen, the similarity in the two substances is evident.

Graphitic acid is usually explosive, but the material produced in the arc burns quietly in the bunsen flame. Dilute acids immediately flocculate the suspended substance, and the gel formed is peptised by repeated washing with water; this property is possessed by graphitic acid, and in addition the appearances of the two in the microscope are similar.

A determination of the heat of combustion of the dried material was made in a bomb calorimeter, giving a result of 8.4 cal. per gram. If it is assumed to be a pure substance of the formula $C_{11}H_4O_5$, then the heat of formation is about 1800 cal. per gram mol (positive). No data could be found on the heat of formation of graphitic acid.

(b) **Metal Electrodes.**—Electrodes of aluminium, copper, zinc, and iron yield solid substances colloidal in character but not sols, and closely resembling that from the carbon electrodes except in colour.

The copper compound is probably a hydrated hydroxide, mixed with hydrated oxides. It is a blue-green substance and is completely soluble in ammonium hydroxide and HCl, thus resembling cupric hydroxide. Prolonged boiling, however, has little effect, and this treatment turns cupric hydroxide black. The solution is distinctly alkaline with p_H 8.5 when saturated, and gives tests for dissolved copper. Colorimetric determination gave 16 mg. of copper per litre as the solubility, but no data could be found as to the solubility of cupric hydroxide.

The zinc compound is partially soluble in ammonium hydroxide and acids, but is flocculated by these reagents; it is soluble in ammonium chloride, and is probably a hydrated hydroxide or oxide similar to

²⁹ Mellor: *Comprehensive Treatise on Inorg. Chem.*, Vol. II., p. 825 (Graphitic acid); Vol. IV., p. 521 (Zinc hydroxide); Vol. II., p. 904 (Carbon suboxides).

^{29a} Hulett and Nelson, trans. *Am. Electrochem. Soc.*, **37**, 103, 1920.

"zinc hydroxide" which Mellor²⁰ shows is not definitely a compound. A saturated solution of the substance is alkaline with p_H 7.6 approximately.

The hydroxide nature of the compounds from the metal electrodes seems established, and possibly the carbon compound is similarly constituted. At any rate all of the oxygen in the latter cannot be due merely to water of hydration, because of the proportions of hydrogen and oxygen occurring here; the existence of a compound resembling graphitic acid, regardless of its exact composition, indicated that the hydrogen-oxygen balance could not be obtained by consideration of the gaseous products alone. This will be discussed later.

5. Soluble Substances Produced in the Discharge.

Fresh solutions from arcing carbon and metal electrodes in boiled distilled water gave no tests for hydrogen peroxide, ozone, aldehyde, or ketone, and no definite iodoform reaction.

After several minutes arcing in pure distilled water vigorous electrolysis always occurred when the electrodes were separated, *i.e.* the conductivity of the water was greatly increased. The hydrogen-ion concentration of solutions in which various electrodes had been arcing was therefore taken, and the results are given below; the "core" relates to soft carbon electrodes employed in ultra-violet therapy work, and the metals are present as oxides. All solutions were originally neutral with p_H 7.0.

Core Substance.	p_H Value when Saturated.
Uncored hard carbon	6.0
Uncored soft carbon	5.8
Cerium core	3.0
Fe, Al, Ni, Si	6.0

The solutions reached these values after three minutes arcing in 200 c.c. water, the voltage being about 30 volts and the current 15 amps.; the water was kept boiling to prevent dissolving of carbon dioxide.

As stated previously, arcing will not take place in strongly acidic or basic solutions, but weak acids such as boric do not inhibit arcing. The arc with zinc electrodes changes the p_H of 200 c.c. of a boric acid solution from 5.0 to 7.5 after five minutes arcing, but in such solution the flocculent zinc compound discussed above is apparently not formed, only a heavy black amorphous substance settling out.

Evaporation of the filtered solution from metal electrode arcs revealed traces of the metal and the "hydroxide" compounds, while the same treatment of the liquid from the carbon arcs gave an almost white powder, evidently not the carbon compound previously described. This substance was insoluble in ether, somewhat soluble in water, and readily soluble in small amounts of ethyl alcohol. It melts above 350° C. but below a red heat.

The water solution of the substance was quite acidic, giving a p_H value of 4.0. It is therefore probably an acid such as mellitic or pyromellitic produced by the solution of higher oxides of carbon, some of which are anhydrides of these acids; such oxides are produced in many types of electrical discharges, as mentioned by Mellor.²⁰ The fact that the substance gives a p_H of 4, compared to a p_H of 6, for the mixture of this, and the solid carbon compound, may indicate that the latter is basic in character, as suggested previously.

Distillation of the clear filtered liquid from carbon arcs failed to show the presence of any volatile substances; similar results were obtained by Fowler and Mardles²⁰ with sparks in organic liquids, and these workers also obtained a solid substance of high melting-point.

Since the carbon arc under pure water gives the gaseous, solid, and soluble substances outlined above, in order to determine the mass relationships in the reactions taking place, all these products must be considered. An apparatus is now being constructed with which this problem may be fully investigated. It is clear, however, that there exists no "water gas" equilibrium as was formerly thought to be the case, and that the reaction is not a simple thermal one between the carbon electrodes and the steam produced in the arc.

The remainder of this paper deals with experiments done with a view to determining the mechanism of the reactions taking place in the carbon electrode arc under water.

6. Effect of Temperature of the Water upon the Reaction.

A rise in the temperature of the water was always observed to result in an apparent increase in the gas produced by the arc in a given time, regardless of the electrode material. Since the gas flow is a measure of the velocity of the reaction or reactions taking place, the above effect was measured accurately. As the temperature of the water approached the boiling-point the vapour pressure rose rapidly and the evolved gas mixture became richer in water vapour. Since the heat supply was constant, that is, there was a constant rate of input energy, the evolution of water vapour depended directly upon the vapour pressure. To determine whether the apparent increase in gas flow was merely due to this effect a series of tests were made in which the gas-water vapour mixture was collected and measured at the temperature of the water itself. The arc with hard carbon electrodes was operated in a large vessel, the temperature of the water being regulated to within 1° C. by means of an electric heating coil, and the gas was collected by displacement of water in a measuring cylinder held above the arc. The measuring error was less than 2 per cent. and to average the errors due to variation in the arc operation ten or more tests were run at each temperature. The arc was hand operated, as this gives the most consistent results, and the runs were for one to five minutes, depending upon the volume of gas evolved.

Fig. 1 gives the results of these tests in graphic form, the data being in Table II. With the curve is given the vapour pressure curve of water (same abscissæ). It is seen that the increase in gas flow is not entirely accounted for by the increase in the partial pressure of the water in the gas mixtures collected.

TABLE II.

Water Temperature.	Gas Flow. c.c./min.	Water Temperature.	Gas Flow. c.c./min.	Water Temperature.	Gas Flow. c.c./min.
4° C.	225	41° C.	375	75° C.	410
7°	225	43°	300	82°	450
13°	210	52°	375	83°	600
16°	250	55°	400	85°	650
20°	300	61°	410	90°	1100
26°	260	63°	390	91°	1250
29°	325	70°	400	97°	2900
34°	275				

An apparatus similar to that discussed in Section 2, but much larger, and constructed of iron pipe instead of sheet copper, was used to verify the above conclusion. The electrodes were mounted horizontally through the ends of a 2-ft. length of pipe (4 ins. in diameter). At the centre of this a second length of pipe was fixed vertically, so that the whole took the form of an inverted T. The water was electrically

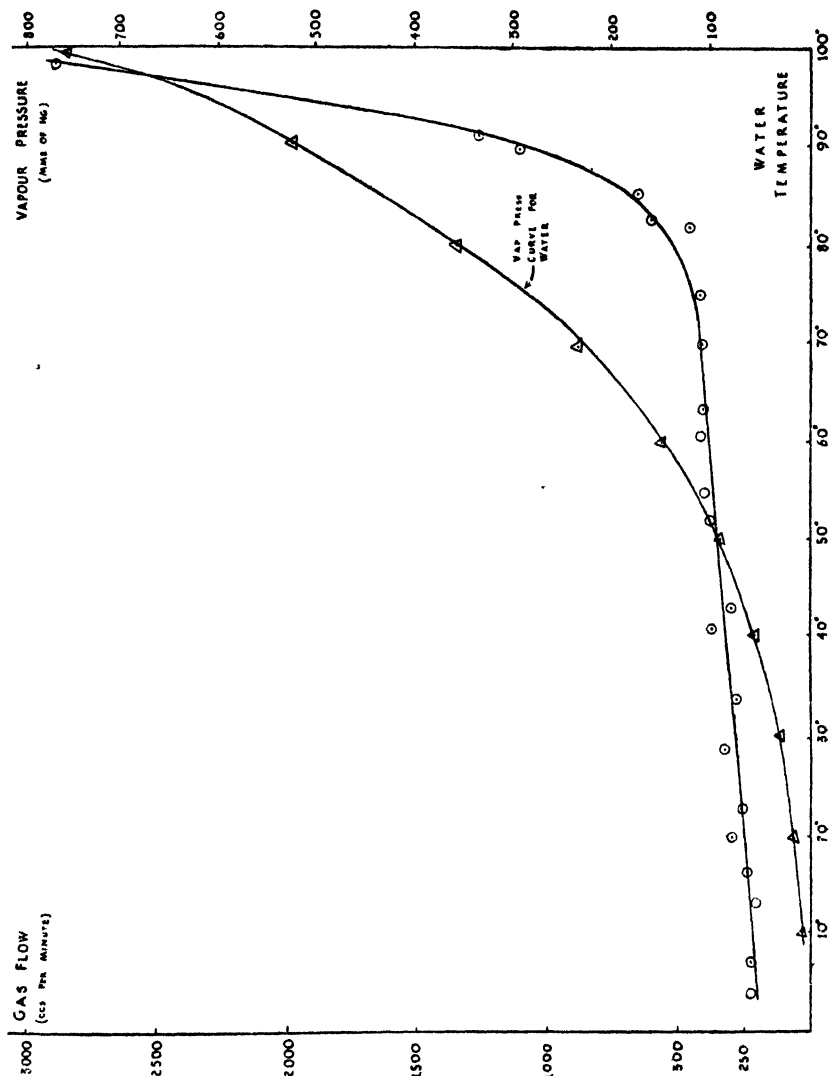


Fig. 1

heated and the gas passed from the apparatus through a condenser to a cooling vessel, being finally collected over water at a fixed temperature. In this way the gas was measured under constant temperature and pressure conditions, regardless of the temperature of the water in which the arc operated. The results are shown in Fig. 2; there is a considerable increase in the rate of the reaction as the water temperature approaches the boiling-point, the curve indicating that past

100° C. or so there is little further rise. Tests were not continued past this point because of the pressure required. The data used in the curve are given in Table III.

TABLE III.

Water Temperature.	Gas Flow, c.c./min.	Water Temperature.	Gas Flow, c.c./min.	Water Temperature.	Gas Flow, c.c./min.
10° C.	200	40° C.	220	90° C.	320
18°	210	60°	235	100°	340
27°	200	70°	260	110°	360
36°	225	80°	270	120°	370
42°	230				

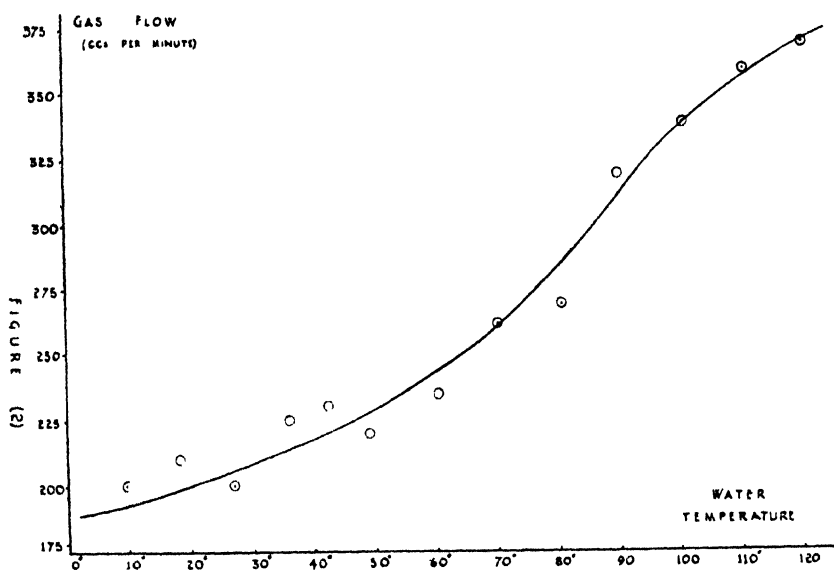


FIG. 2

7. Measurement of the Arc Temperature.

Many measurements have been made of the temperature of arcs in air and various gases, but no similar data have been found relating to arcs in liquids. However, Wilson³⁰ has determined the temperature of under-water sparks with an applied potential of 20,000 volts; spectra measurements involving Birge's formula and based on the quantum theory gave the temperature in this case as 5115° C., which was claimed to be accurate. It was desirable to measure the temperature of the arcs used in this work with a view to determining whether or not the reactions were purely thermal in nature.

There are available several methods of measuring high temperatures, discussed by Mason³¹ and Tanberg and Berkey.³² In the latter paper it is shown that a very accurate method gave results close to those

³⁰ Wilson, *J. Opt. Soc. Am.*, **17**, 37, 1928.

³¹ Mason, *Physic. Rev.*, **38**, 427, 1931.

³² Tanberg and Berkey, *Physic. Rev.*, **38**, 296, 1931.

secured with an optical pyrometer, and the accuracy of the latter instrument is discussed.

In the following a "Holborn and Kurlbaum" type of optical pyrometer was used, manufactured by Leeds and Northrup. Since the calibration supplied did not extend into the temperature regions measured, it was necessary to increase the range. With this type of instrument a neutral absorption "filter" may be employed, and extrapolation from the known calibration curve carried out, employing Wien's law in modified form.

Calibration of such a neutral white glass filter was carried up to 2000°C. , a smooth curve being obtained. Then the carbon arc in air was measured, and its temperature taken as 3500°C. , this being the accepted value for the crater. The curve could then be continued to this point, and to verify the soundness of this method the formula of Pirani and Meyer, as cited by Burgess and Le Chatelier,³³ was applied. It was found to agree to within 100° (maximum error), and this accuracy was sufficient since comparative temperatures rather than absolute values were desired.

The arcs were operated in a litre of water contained in a copper vessel fitted with a small window of extremely thin sheet mica. The arc was hand-operated with horizontally opposed electrodes held close to the window, and all measurements were made with the pyrometer the same distance from the arc as from the calibration sources. Because of the small size of the arc region it was not possible to discriminate between cathode and anode temperatures. The arc was viewed at right angles to the electrodes and no difference in temperature throughout the brilliant source spot could be detected by the instrument. It is therefore evident that whatever temperature gradient may exist in these arcs, the mean temperature throughout was the value measured.

Three groups of tests were carried out: first, the effect of the temperature of the water upon the arc temperature, with constant voltage applied to the arc. Second, the effect of increasing the applied voltage on the temperature of the arc, the temperature of the water being $25\text{--}30^{\circ}\text{C.}$, and third, the same effect with the water temperature at 100°C. , *i.e.* boiling vigorously. The voltages given on the curves of Fig. 3 were the average figures read on the instruments and, of course, did not take into account wide fluctuations which occur momentarily, *i.e.* they are not "mean" voltages. The latter figures would have had no significance since the temperatures were measured during steady arc operation.

Fig. 3 shows five curves plotted from the data in Table IV., each for a different type of carbon electrode, many of them with metal oxide cores. It is seen that a 1500° rise in the arc temperature is the general effect when the temperature of the water is raised from 5° to 100°C. ; the significance of this will be discussed later.

In the following table and curves the clarendon letters used indicate the type of carbon employed, as follows:—

Lettering.	Type of Carbon.
A	Soft, cerium core.
B	Hard, no core.
C	Soft, Al, Ni, Fe, Si core.
D	Soft, no core.

³³ Burgess and Le Chatelier: *High Temperature Measurement*, p. 328 (Wiley & Sons), 1912.

TABLE IV.

Water Temperature.	Arc Temperature.	Water Temperature.	Arc Temperature.
B.		A.	
8° C.	1325° C.	11° C.	2300° C.
60°	2025°	25°	2525°
100°	2500°	100°	2725°
D.		C.	
14° C.	2300° C.	8° C.	2700° C.
25°	2500°	25°	2750°
100°	2925°	100°	3625°

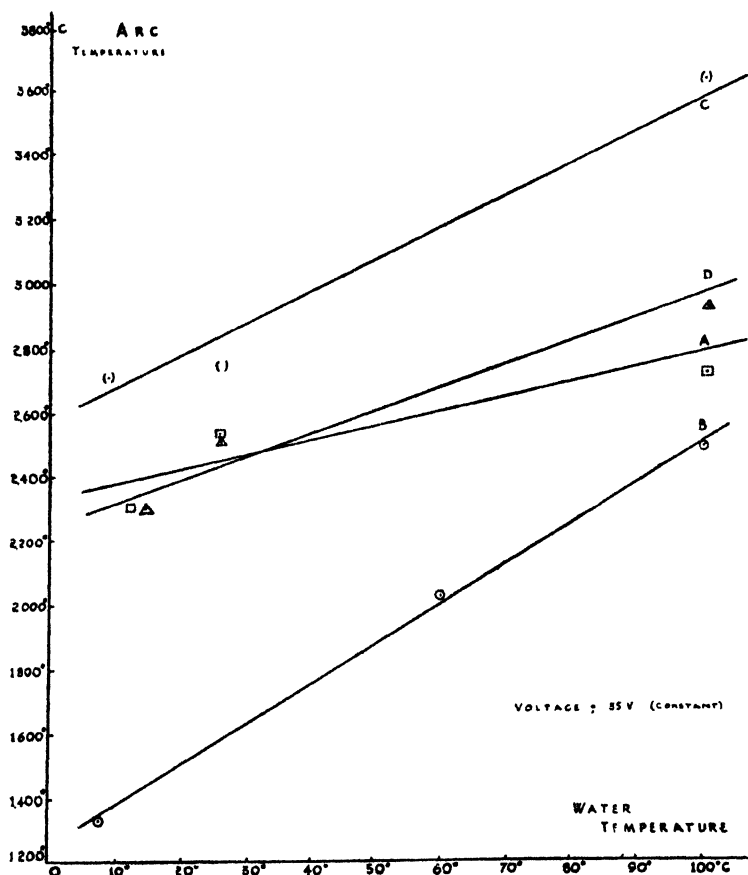


FIG. 3.

The relationships between the arc temperature and the voltage were also determined, and will be reported when the corresponding effects on the reactions have been found.

The lowest temperature measured was 1300° C. with a hard uncured carbon arc at 25 volts, the water temperature being 8° C. Soft

"graphite" electrodes with a strontium core gave the highest temperature, *viz.* 3600°C ., arcing at 40 volts with the water boiling. Some thirty measurements were made between these two extremes, in steps of 75° . The core substances have little effect upon the arc temperature, but the latter is greatly affected by the quality of carbon. Under the same conditions of voltage and water temperature the hard or "projector" carbons gave the lowest, and the soft or "graphite" carbons the highest temperature readings.

Since the sensitivity of the instrument used was lessened by the addition of the neutral filter, the temperatures read have probably a maximum error of 100°C . It is not unlikely that the high temperatures measured were actually somewhat lower than the true arc temperatures, since the water diffused the light considerably, and no correction was made for this. The temperature of the air arc used in calibrating the instrument, *viz.* 3500°C ., was obtained with pure uncored carbon rods and a low D.C. voltage; hence the fact that a temperature of 3600°C . was obtained with cored graphite rods under water, with a higher voltage than the above, does not show that the under-water measurements are in error, for cored rods of this sort are known to give a much higher temperature arc than uncored types. Attempts are now being made to determine the temperatures of the various under-water arcs by measurements of their continuous spectra.

8. Effect of Pressure on Arcing.

Shipley and Goodeve,¹⁸ working with arcs in boiling alkaline electrolytes, found that 3 lb. per sq. in. pressure above atmospheric inhibited

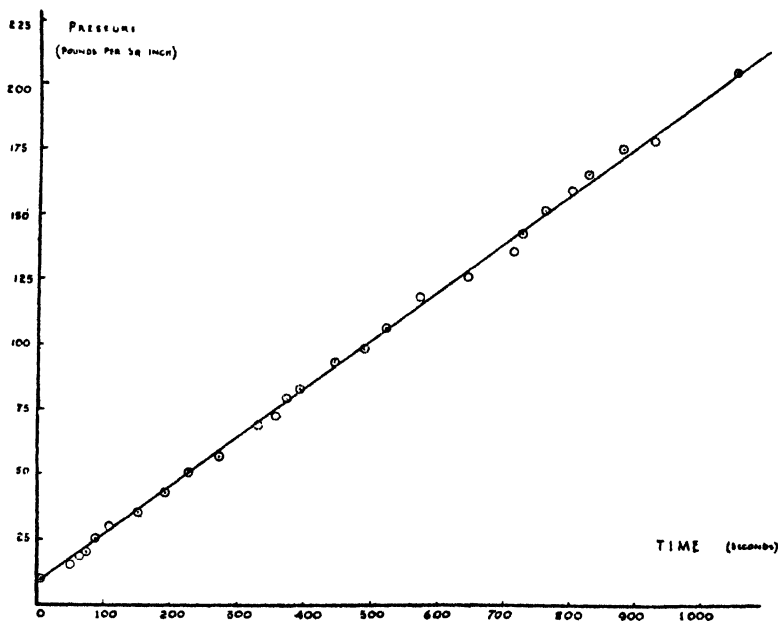


FIG. 4.

all arcing with an applied potential of 700 volts A.C., while 31 lb. suppressed arcing with 2200 volts applied. It was thought that the

arcs dealt with in this paper, *i.e.* "struck" arcs in water of low conductivity, were entirely different in mechanism and in products to those discussed in the above reference. To verify this the effect of pressure on the arc with carbon electrodes was determined.

The apparatus was practically the same as that used in determining the effect of water temperature (Section 6), being strengthened to stand high pressures. The adjustable electrode was fed in by means of a screw thread, the sealing arrangement being similar to that used in high pressure valves. The arcs were operated at 30 volts, the current being about 15 amps., and the connections to the electrodes were made from the outside by means of heavy automobile "spark plugs," slightly altered.

In a closed system such as this a constant rise in pressure per unit time indicates a constant mass of gas produced in that time, assuming the Gas Laws to hold. Fig. 4 shows the rise in pressure against time, readings being taken about four times per minute, and the data is in Table V. The curve is quite linear, showing that the amount of gas produced was independent of the pressure within the limits used.

TABLE V.

Time. Seconds.	Pressure. (lb./sq. in.)	Time. Seconds.	Pressure. (lb./sq. in.)	Time. Seconds.	Pressure. (lb./sq. in.)
0	10	340	68	720	135
50	15	360	72	730	141
60	17	375	77	770	152
75	20	395	85	810	158
110	30	450	92	835	165
145	35	495	98	880	175
195	42	525	106	940	180
230	50	575	118	1040	205
275	57	650	125		

To verify the above conclusion, tests were run at pressures throughout the range of Table V., in which the gas evolved was expanded to atmospheric pressure and its volume measured at constant temperature. The highest pressure employed was 350 lb./sq. in. or about 23 atmospheres. Regardless of the pressure the volume of gas evolved per unit time did not vary more than 5 per cent. from the mean, and there was no regularity in the fluctuation.

At pressures over five atmospheres the characteristics of the arc underwent some changes; the sound emitted, and the mechanical vibration of the heavy apparatus (weight about 75 lb.) increased greatly. This effect lessened and finally disappeared when the pressure was increased to eight atmospheres. Visual observation of the arc indicated little change, but this was not conclusive because of the heavy protective glass lenses used, the latter being set into the side of the apparatus.

It is evident, however, that pressure has little if any effect upon the production of gaseous products, and as this latter factor may be taken as a measure of the reactions taking place, it may have some bearing upon the mechanism.

Theoretical Considerations.

The earliest workers in the field of electric discharges in liquids and gases found the theory of "electrolysis" to be untenable, because of

the disagreement with Faraday's law, but Chapman and Lidbury,¹⁸ with others, made use of the term "electrolysis of steam." In 1900 Löb⁸ realised that the electrodes had a great influence upon the arcing itself, and upon the gaseous products; and we have shown that the formation of soluble and insoluble solid carbon compounds in addition to the gaseous products, complicates the study of the carbon arc under water.

The question arises as to whether the reaction is not a simple one between the steam produced in the arc and the carbon at the high temperatures which have been shown to exist. Pring and Hutton³⁴ investigated the reaction between hydrogen and carbon heated to a high temperature by an electric current, and found acetylene produced in increasing amounts as the temperature was raised; but the irregular results observed and the methods of analysis employed leave doubts as to whether the acetylene was a direct product of the reaction or due to impurities in the carbon. At any rate, with steam and carbon the reaction is quite different, and Thiele and Haslam³⁵ have shown the "water gas" reaction to be somewhat complicated, involving surface reactions. No electrical influences were employed in this work, and no mention is made of saturated or unsaturated hydrocarbons being produced.

Influence of the Water.—With the arc in liquid water a high temperature is produced when the electrodes are brought together, due to the great resistance of the irregular ends, and the formation of steam follows immediately. The arcing no doubt takes place in the steam, but separation of the electrodes is not necessary to secure arcing, as discussed previously. With a given power input to the arc the extent of the steam "mantle" would depend upon the temperature of the surrounding water, as this affects the rapidity with which the steam condenses as it leaves the arc due to the buoyancy effect. As long as the arc is surrounded by steam a region of very high temperature can be produced and maintained because of the low heat conductivity of the steam; the sweeping effect of the evolved gases would tend to remove the steam from the upper part of the arc.

It is thus seen how a rise of 75° in the temperature of the water can result in a 1500° rise in the arc temperature: as the boiling-point is approached the steam is removed much less rapidly from the arc region. In addition to this it must be considered that less energy is required to heat the water up to boiling, and this factor must be of considerable importance when the large amount of steam produced in the arc is taken into account, because this steam is rapidly condensed by the surrounding liquid. More energy is available for chemical reactions when the water is near the boiling-point, whether these be purely thermal due to the high temperature or of some other nature; this may explain the rise exhibited in Fig. 2.

Nature of the Reactions.—The dissociation of water vapour into its elements at high temperatures has been studied by Lowenstein,³⁶ Langmuir,³⁷ and others, and the appreciable extent of the dissociation over 2000° C. has been established. Bjerrum³⁸ has carried out these

³⁴ Pring and Hutton, *J. Chem. Soc.*, 89, 1591, 1906.

³⁵ Thiele and Haslam, *J. Ind. Eng. Chem.*, 19, 882, 1927.

³⁶ Lowenstein, *Z. physik. Chem.*, 54, 797, 1905; 56, 513, 1906.

³⁷ Langmuir, *J. Am. Chem. Soc.*, 28, 1351, 1906.

³⁸ Bjerrum, *Z. physik. Chem.*, 79, 513, 1912.

investigations up to nearly 3000° C. and observed at the latter temperature over 11 per cent. dissociation; these results, obtained by the bomb method, agree well with those for lower temperatures. It is possible therefore that the preliminary reaction in the arc is the thermal decomposition of the steam into hydrogen and oxygen at the high temperatures obtaining here.

The possibility that the primary reaction is of the "water gas" type is evident, but the existing data on this equilibrium would tend to disprove this. Haber³⁹ gives a review of this work, and the percentage composition of the gases do not correspond at all to those from the arc, for similar temperatures. The existence of solid products is a further indication that there is no such simple equilibrium in the arc.

It is theoretically possible that the thermal decomposition of the steam, with subsequent union of the oxygen with the electrodes to produce gaseous and solid carbon oxide, constitutes the entire mechanism of the reactions. If this were true an increase in the temperature of the arc should result in a corresponding increase in the reaction velocity, the latter rising rapidly past 2000° C. A consideration of Figs. 2 and 3 will show that the increase in gas flow as the water temperature rises is not accounted for by the accompanying increase in the arc temperature. Certain qualitative experiments, now being repeated carefully, indicate that the reaction is to a large extent governed by the applied voltage, and this points to an ionisation effect.

There is a space potential gradient in these arcs amounting to at least 300 volts per cm. when 30 volts are applied to the electrodes, the length of the arc being less than a millimetre. This potential is sufficient to produce a large variety of ions from substances available in the arc, as shown by Senftleben and Rehren,⁴⁰ and Bleakney.⁴¹

The electric discharge through water vapour has been known to produce the so-called "water" bands and lines, and Konen⁶ has observed these with certain under-water arcs. Watson⁴² has recently shown these bands to be due to the OH ion, and Barton and Bartlett⁴³ have shown how extensive the production of these ions is. Lozier⁴⁴ considers that the formation of the OH particle is a step in the dissociation of water vapour, and considering these facts it is possible that the most important preliminary reaction taking place in the under-water arc is the dissociation of water into H and OH particles. These may be charged during formation, or subsequently by the electron stream in the arc, and thus be given a high kinetic energy by the potential gradient existing between the electrodes. In this condition they would be capable of bringing about similar dissociation of other water molecules.

We consider that it is probable that the OH particles, which may be charged and highly excited, react directly with the electrode materials, forming metal hydroxides with copper, zinc, and other electrodes, and a "graphitic acid" type of compound with carbon electrodes. It is significant that no more than traces of free oxygen escape from the arc, as this would hardly be the case if the dissociation of water vapour were

³⁹ Haber, *Thermodynamics of Technical Gas Reactions* (trans. by Lamb), p. 122, 1908; *Oxygen-hydrogen reaction*, p. 177.

⁴⁰ Senftleben and Rehren, *Z. Physik*, **37**, 529, 1926; Also Senftleben, *Z. Physik*, **37**, 539, 1926.

⁴¹ Bleakney, *Physic. Rev.*, **35**, 1180, 1930.

⁴² Watson, *Astrophys. J.*, **60**, 145, 1924.

⁴³ Barton and Bartlett, *Physic. Rev.*, **31**, 823, 1928.

⁴⁴ Lozier, *Physic. Rev.*, **36**, 1417, 1930.

purely thermal, the equilibrium being "frozen" by the surrounding cold liquid. The fact that the oxygen is all in chemical union with the electrode material may indicate that the predominant reaction is electrical in nature, taking place on the electrode surface, or in the regions of great potential fall (amounting to millions of volts per cm.) which have been shown by Mason ⁴⁵ and others to exist close to arc electrodes. However, the purely thermal dissociation of the water must play some part, whether accompanied by electrical effects or not.

There is also the possibility that photochemical reactions play a part in these arcs, since under-water discharges have long been known to be sources of intense, low wave-length radiations. This point will be investigated later, when a search is made for further products, and some spectral evidence secured.

Energy relationship between the electrical input and thermal energy output are being studied, and in this connection there has been found much conflicting data as to the heat of formation of water from its elements, at high temperatures. Haber and Bruner ⁴⁶ found the heat of formation to decrease with rise in temperature, while Haber ³⁹ reviews evidence to the contrary. The disagreement with thermodynamical theory would seem to lie in lack of accurate data on the variation of the specific heats of oxygen, hydrogen and water vapour at high temperatures; Bjerrum ³⁸ has shown this variation in the case of hydrogen to be considerable.

Summary.

A special type of low voltage contact arc, operating under water, is described. The chemical nature of the gaseous, liquid, and solid products is examined in detail. With regard to gaseous products, the results of previous workers are qualitatively but not quantitatively confirmed, and considerable attention is given to a gaseous inactive residue. The solid products are shown to be hydroxidic in character; the solid product from carbon arcs is shown to be a body of the nature of graphitic acid; in the latter case, traces of a sparingly soluble, high-melting acid are simultaneously produced.

The apparent or mean temperatures of the under-water arcs are investigated by means of an optical pyrometer, and their variation with temperature of the surrounding water. The variation of total gaseous yield with temperature and pressure is investigated.

The mechanism of the process is discussed in the light of the results communicated, and the following probabilities are arrived at: (1) The process is not a mere thermal reaction; (2) A certain proportion of the reaction is no doubt due to the fairly considerable dissociation of water vapour at the high temperatures in question, but (3) it is shown that very probably an electrical dissociation of water vapour into H and OH ions is responsible for at least the solid products; (4) Short wave radiation effects are not excluded.

Work is still proceeding on: (1) The spectrum of the arc, and (2) the energy relations.

Thanks are due to Mr. W. R. Carter for invaluable assistance rendered in the work outlined in Sections 6 and 8, and to Professor M. A. Parker for information and advice.

⁴⁵ Mason, *Physic. Rev.*, **38**, 427, 1931.

⁴⁶ Haber and Bruner, *Z. Elektrochem.*, **10**, 697, 1904.

CATALYSIS AND PHOTO-CONDUCTORS.

By F. H. CONSTABLE, M.A., D.Sc., Ph.D., F.I.C., F.Inst.P., and
A. F. H. WARD, M.A., Ph.D.*

Received 10th February, 1932.

In chemical change promoters and catalysts play a considerable part in determining the rate of chemical change both in homogeneous and heterogeneous systems. The photo-conducting solids owe their light sensitive properties to the effect of light in rendering electrons previously incapable of assisting conduction through the mass of the solid, free to give a considerable current under applied electromotive forces. It was thought that foreign substances might play some part in assisting or retarding the effects produced by light on photo-conductors, analogous to that of catalysts in chemical change. An investigation was therefore made on the effect on the light sensitive properties of selenium films of the action of foreign substances soluble in selenium incorporated in them.

The State of the Added Substances in the Selenium Films.

In order to see whether the added substances formed a homogeneous mixture with the selenium it was necessary to study the phase rule of diagrams for the systems, particularly the parts corresponding to high concentrations of selenium. The substances studied were: silver, thallium, bismuth, lead, mercury, zinc, copper, and iron. In many cases close investigation revealed discrepancies between these results and data found in the literature, which often also showed inconsistencies among themselves. It therefore seems of importance to record here, together with the new results obtained, what information is known about the mixtures given above. All these elements form definite compounds with selenium, in some cases only slowly on heating together, and these compounds are to some extent soluble in selenium. Within limits of temperature and concentration two phases may exist in equilibrium—the solution mentioned above (almost entirely selenium) and the pure selenide or a much stronger solution of it in selenium. This second phase may be either solid or liquid.

Selenium-silver.—Much work has been done on this system,¹ and it has been found that up to about 50 per cent. silver there are two phases, the upper pure selenium (melting at 217° C.), and the lower an equimolecular mixture $\text{Ag}_2\text{Se} + \text{Se}$ (melting at 616° C.). This latter is only stable in the presence of an excess of selenium. Experiments made here have shown that the layer melting at 217° C. is not completely pure selenium, but contains a trace of silver, the amount depending upon the temperature. The maximum concentration of silver in this layer produced by heating almost at the boiling-point of selenium, and cooling rapidly, is about 0.2 per cent. Berger² found a maximum concentration of 0.1 per cent. silver. It is difficult to say whether this

* Radiovisor Research Laboratories, Letchworth.

¹ Pélabon, *Ann. Chim. Physique* (7), **25**, 365, 1902; and (8), **17**, 526, 1909; Pelini, *Gazz.*, **45**, 533, 1915; and Friedrich and Leroux, *Metallurgie*, **5**, 355, 1908.

² *Z. anorg. Chem.*, **50**, 445, 1906.

small amount of silver selenide remains in solution on solidifying to vitreous selenium and after annealing. A thin layer of the mixture pressed between a microscope slide and cover slip at a temperature above the melting-point was examined microscopically by transmitted light. Whereas pure selenium gives a clear red film in this way the selenium plus 0.2 per cent. silver had numerous black spots. These might be either silver selenide, which had come out of solution on cooling, or else centres of crystallisation to the metallic form catalysed by the presence of silver selenide. This was observed with many of the metals considered, and this second solid phase was able to influence the electrical properties of the selenium.

Selenium-lead.—This system is similar to that of selenium-silver, a lower layer ($\text{PbSe} + \text{Se}$) melting at 673°C ., and an upper layer, which has been described by Pélabon³ as pure selenium, being formed. It has been found, however, that this may dissolve up to about 1 per cent. lead, and larger quantities may be held in suspension by stirring and rapid cooling.

Selenium-copper.—This also gives two liquid layers, but the upper layer cannot contain more than about 0.2 per cent. copper in solution. The lower layer contains approximately equal amounts of copper and selenium.

Selenium-mercury.—According to Pellini⁴ mercuric selenide dissolves only very slightly in selenium. Solutions up to about 4 per cent. mercury have been made.

Selenium-zinc.—Zinc and selenium unite with difficulty after long heating at the melting-point of selenium. Solutions of the selenide in selenium containing up to 0.84 per cent. zinc have been made, though Chikashige and Kurosaura⁵ reported that the selenide was insoluble either in zinc or selenium.

Selenium-bismuth.—Here two liquid layers are formed similar to selenium-silver and selenium-lead. According to Tomoshige⁶ the upper layer should melt at 161°C . The melting-point has been measured, and up to 4.6 per cent. bismuth remains stationary at 217°C . Microscopic examination of cooled films from the upper layer showed heterogeneity, but on diluting to 0.08 per cent. bismuth or less a second phase did not separate on cooling.

Selenium-thallium.—Up to 20 per cent. thallium could be dissolved in selenium, the melting-point remaining stationary at 217°C . in this region. Attempts to prepare stronger solutions resulted in the separation of a second phase.

Selenium-iron.—The solubility of iron selenide in selenium is extremely small; not more than 0.002 per cent. iron could be made to go into solution. Mixtures containing higher concentrations of iron were made by powdering iron selenide extremely finely in an agate mortar for several hours and mixing in molten selenium with sufficiently rapid stirring and cooling to produce a uniform concentration.

Preparation of Selenium Cells Containing Dissolved Foreign Substances.

Annealing temperatures from 170°C . to 215°C . were used, and the following substances—silver, thallium, bismuth, lead, mercury, zinc, copper and iron—incorporated in amorphous red selenium, employed as the material from which the cell was made.

³ *C.R.*, **144**, 1159, 1905; and **154**, 1414, 1912.

⁴ *Atti R. Accad. Lincei*, (V.), **18**, ii, 211, 1909.

⁵ *Mem. Coll. Sci. Kyoto*, **2**, 245, 1917.

⁶ *Mem. Coll. Sci. Kyoto*, **4**, 55, 1919.

The selenium or mixture was coated on to a sand blasted glass plate with gold electrodes at about 300° C., followed by annealing for 40 minutes in a copper enclosure to ensure uniform temperature. The cell was left to cool, current being turned on later and the cell left in the dark in dry air for 16 to 18 hours before testing the Dark Resistance. Care was taken that no oxides of selenium were present in the film. The plates of glass were chosen 2 inches by 1 inch, and the roughening and coating such that the thin layer of selenium produced over the plate always approximated to the same value (about 12-15 mgm.) in weight. The resistance measured, owing to the construction of the gold electrodes, is that between electrodes 1 mm. apart and 68 cms. long.

Method of Testing Cells.

In considering the properties of the photo-conducting film of selenium mixed with other substances a considerable number of experiments have been made with each mixture and average values of the properties studied taken. When the bridge is kept in the dark, after a sufficient length of time its resistance becomes steady over the period of time required for the tests herein described if a constant voltage is applied, provided that there is no appreciable heating effect from the current passing, and that good contact is maintained with the cell. If light is then shone on the grid the current increases very rapidly for at most a few seconds and then proceeds to fall. This fall is at first fairly rapid; it then becomes slower, and after some hours a steady value is reached, the current still being larger than its original dark value. If now the light is turned out an immediate rapid fall of current occurs, not completely to the original value of the current passing in the dark but to an intermediate value higher than the original dark reading of the resistance of the bridge. The current then continues to fall gradually to the value that it had before illumination.

On account of the influence of the conditions of preparation and measurement on the properties of the grid the measurements which are considered in this paper were carefully standardised. The Dark Resistance of the grid was taken after 16 to 18 hours in the dark with the current flowing at 250 volts D.C., and was the value taken in the further experiments for the dark resistance, experiments showing that this value was not appreciably altered if the bridge had remained in the dark during the time required for the further light tests. The Light Ratio is defined as the $\frac{\text{current in the light}}{\text{current in the dark}}$. In this ratio the Light Current varies considerably during the first few hours of illumination at constant intensity, and more accurate definition is required. We have considered three different Light Ratios—the Instantaneous Light Ratio, the Terminal Light Ratio, and the Decay Light Ratio—in order to classify the grids roughly. The Instantaneous Light Ratio is the ratio of the current to the dark current 1 minute after the light has been turned on; the Terminal Light Ratio has as the numerator in the ratio the light current which is finally reached after several hours; and the Decay Light Ratio is the ratio of the final steady light current to the dark current reached 1 minute after the light has been turned out. In all cases a light intensity of 100 lux was used. These experiments were carried out in the temperature range 10° C. to 20° C. The effect of:

- (1) variation in annealing temperature; and
- (2) various concentrations of added substances,

on the Dark Resistance and Light Ratios of batches of selenium cells were observed, and the median values taken.

The Behaviour of Pure Selenium.

In general the higher the temperature at which a selenium film is annealed the lower the value of the Dark Resistance obtained. There is, however, variation in the properties of a series of bridges annealed at any one temperature, caused by the random nature of the crystallisation process itself, and hence all observations recorded are the median of a group of observations. The average results for pure selenium cells made under the conditions of these experiments are shown in Figs. 1

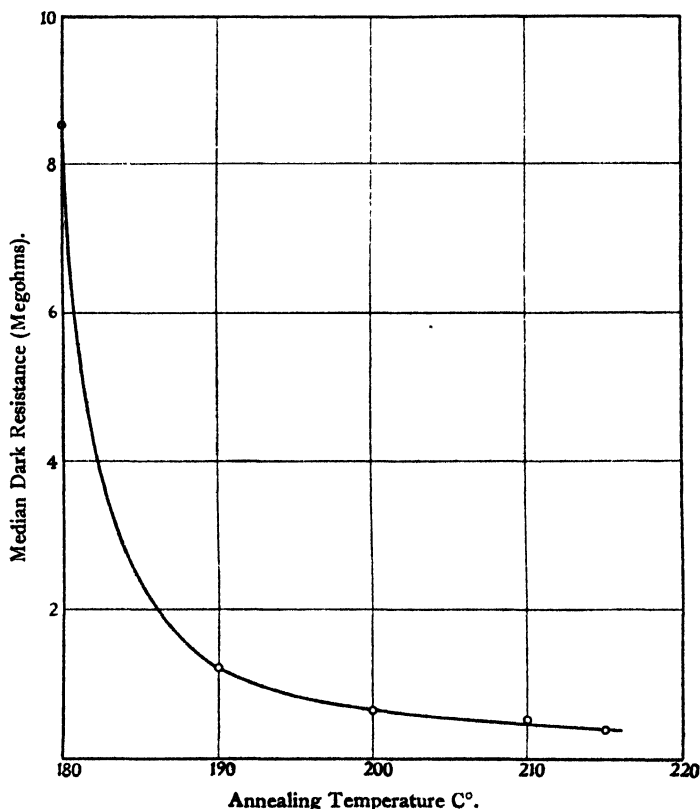


FIG. 1.—Median Resistances and Annealing Temperatures.

and 2. In the case of bridges prepared as above, the Dark Resistance of bridges annealed at 180° C. is of the order of 10 megohms. The values fall as the temperature rises, and at about 200° C. annealing the value of the resistance is of the order of 0.5 megohm. The various Light Ratios vary correspondingly with the annealing temperature. In general it can be stated that the higher the resistance the higher the Light Ratio; that is, the grids made at the lowest annealing temperature will have the highest Light Ratios. Graphs have been plotted for Light Ratio against Resistance and, in spite of the variation in resistance that occurs at any single annealing temperature, smooth curves have been obtained from median observation taken early in the life of the bridge and at a corresponding time to that at which the measurements for the alloys

were taken. This means that if a bridge at high annealing temperature (say 210° C.) has an unduly high resistance—say a resistance which might be normal for a bridge annealed at 190° C.—it would normally have a correspondingly high Light Ratio, the value that would have been expected for the normal Light Ratio at 190° C., unless it had developed a path or paths of low conductivity between two electrodes of the grid. If the various median Light Ratios are plotted against the logarithm of

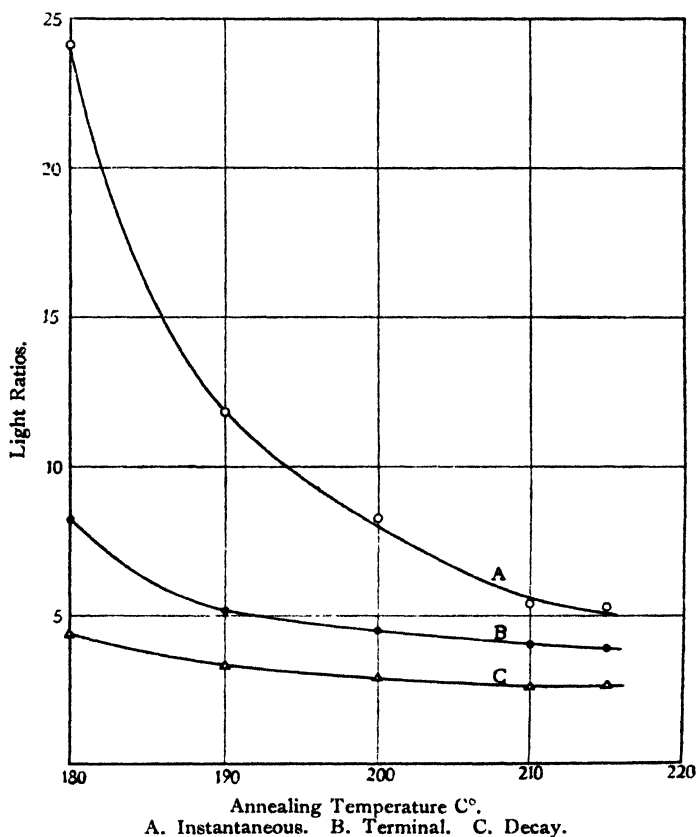


FIG. 2.—Median results showing Variation of Light Ratios with Annealing Temperatures.

the Resistance straight lines are obtained, which means that the median Light Ratio of a group of bridges is connected with the Resistance by an equation of the form — $L.R. = x + y \log R$ over this range of temperature. When Resistances are expressed in megohms and logarithms are taken to base 10 the constants x and y have the following values in this early period in the life of the bridge.

	x .	y .
Instantaneous L.R. . . .	2.50	36.50
Terminal L.R.	4.25	4.80
Decay L.R.	2.62	2.60

The figures for all bridges do not fall accurately on this same straight line; there is random variation, but as the result of testing several

hundreds of bridges in this way the above equation may be considered to express satisfactorily the average relationship. The cause of this variation in properties of selenium bridges cannot be due to variation of annealing temperature in different parts of the furnace since the variation obtained in one batch of annealed bridges is very much greater than would be expected from the maximum possible temperature variation in the oven. The most probable explanation is that owing to the fact that the selenium bridge consists of a conglomeration of small crystals the major part of the resistance is probably due to contact resistance between the different crystals, so that the final value of the resistance will depend on the distribution of the original centres of crystallisation, which cannot be controlled.⁷ The method of investigation used avoided this difficulty by the use of comparative methods and statistical means, and so obtaining median observations on groups of bridges made with any one alloy. Further, unless the results showed changes in properties large compared with the median variation with pure selenium they were disregarded. The values given for pure selenium in the following tables are blank experiments conducted in the same way as with the alloy.

Results of Additions of Foreign Substances on the Light Sensitive Properties.

(1) Substances decreasing the Dark Resistance and Light Ratios.

The results obtained for mixtures of iron selenide and selenium are below :—

TABLE I.—SELENIUM-IRON. (40 mins. annealing.)

	Annealing Temperature (°C.).	Median Dark Resistance (megohms).	Median Values in White Light (100 lux).		
			Instantaneous Light Ratio.	Terminal Light Ratio.	Decay Light Ratio.
Alloys—					
0.013 % Fe .	170	8.5	26.0	7.4	6.5
0.031 % Fe .		6.1	22.5	7.1	6.0
3.2 % Fe .		2.9	11.1	3.8	3.8
6.0 % Fe .		0.60	4.6	2.2	2.1
Pure selenium .		8.9	27.0	7.0	5.3
Alloys—					
0.013 % Fe .	180	7.2	22.0	7.2	5.0
0.031 % Fe .		6.3	26.5	7.8	5.5
3.2 % Fe .		1.3	7.1	2.7	2.7
6.0 % Fe .		1.1	5.3	3.0	2.8
Pure selenium .		7.1	19.5	9.0	4.5
Alloys—					
0.013 % Fe .	190	2.1	18.5	9.0	3.9
0.031 % Fe .		2.0	14.0	6.0	4.3
3.2 % Fe .		0.33	4.4	2.1	2.6
6.0 % Fe .		0.54	4.6	1.7	2.0
Pure selenium .		1.7	14.0	5.0	3.7
Alloys—					
0.013 % Fe .	200	0.89	11.7	6.3	3.6
0.031 % Fe .		0.32	5.6	3.4	3.1
3.2 % Fe .		0.21	2.5	1.8	2.1
6.0 % Fe .		0.26	3.1	1.9	2.2
Pure selenium .		0.70	9.5	5.1	3.3

⁷ Cf. Brown and Sieg, *Physical Rev.* (2), 4, 48, 1914.

TABLE I.—SELENIUM-IRON. (40 mins. annealing.)—*Continued.*

	Annealing Temperature (°C.).	Median Dark Resistance (megohms).	Median Values in White Light (100 Lux).		
			Instantaneous Light Ratio.	Terminal Light Ratio.	Decay Light Ratio.
Alloys—					
0.013 % Fe .	210	0.59	7.4	4.5	3.4
0.031 % Fe .		0.33	4.4	3.2	2.8
3.2 % Fe .		0.24	2.6	1.9	2.0
6.0 % Fe .		0.20	2.7	1.2	1.9
Pure selenium .		0.36	4.6	3.0	2.7
Alloys—					
0.013 % Fe .	215	0.93	7.4	5.0	3.8
0.031 % Fe .		0.63	6.2	5.0	3.3
3.2 % Fe .		0.15	2.7	2.0	1.9
6.0 % Fe .		0.23	2.5	1.8	1.8
Pure selenium .		0.52	6.3	4.3	3.1

It is evident that while a very small proportion of iron has little effect, as the concentration increases the Dark Resistance is markedly depressed, this being mostly so at the lower annealing temperatures ; in addition the Light Ratios are depressed.

(2) *Substances which are indifferent.*

As seen in Tables II. and III. below, both zinc and lead have little influence on the Resistance or the light sensitivity of the selenium films.

TABLE II.—SELENIUM-ZINC. (40 mins. annealing.)

	Annealing Temperature (°C.).	Median Dark Resistance (megohms).	Median Values in White Light (100 lux).		
			Instantaneous Light Ratio.	Terminal Light Ratio.	Decay Light Ratio.
Alloys—					
0.004 % Zn .	180	6.6	32.0	11.1	4.7
0.25 % Zn .		3.0	24.0	8.8	5.3
0.85 % Zn .		4.3	26.0	8.3	5.3
Pure selenium .		8.3	33.0	11.7	4.7
Alloys—					
0.004 % Zn .	190	0.55	8.0	5.0	3.1
0.25 % Zn .		1.29	13.4	8.0	4.2
0.85 % Zn .		1.6	13.0	9.4	3.8
Pure selenium .		0.77	10.3	5.9	3.2
Alloys—					
0.004 % Zn .	200	0.24	5.3	3.6	2.2
0.25 % Zn .		0.51	8.1	6.7	3.3
0.85 % Zn .		0.37	5.9	4.9	3.8
Pure selenium .		0.12	3.3	2.5	1.9
Alloys—					
0.004 % Zn .	210	0.99	11.7	9.6	3.3
0.25 % Zn .		0.22	4.3	3.5	2.4
0.85 % Zn .		0.45	5.4	4.8	2.8
Pure selenium .		0.71	10.0	8.1	2.9
Alloys—					
0.004 % Zn .	215	0.63	7.5	6.0	3.2
0.25 % Zn .		0.50	7.4	6.6	3.4
0.85 % Zn .		0.40	6.9	5.8	2.9
Pure selenium .		0.38	6.9	5.1	2.7

TABLE III.—SELENIUM-LEAD. (40 mins. annealing.)

	Annealing Temperature (°C.).	Median Dark Resistance (megohms).	Median Values in White Light (100 lux).		
			Instantaneous Light Ratio.	Terminal Light Ratio.	Decay Light Ratio.
Alloys—					
0.06 % Pb . . .	180	13.9	13.0	5.8	3.8
1.0 % Pb . . .		4.5	19.0	9.3	5.6
2.3 % Pb . . .		4.0	15.0	7.0	5.3
Pure selenium . .		5.2	24.0	9.4	4.5
Alloys—					
0.06 % Pb . . .	190	0.74	8.2	2.5	3.4
1.0 % Pb . . .		1.35	8.2	3.3	2.8
2.3 % Pb . . .		1.4	10.2	2.8	4.1
Pure selenium . .		0.61	7.6	2.7	2.6
Alloys—					
0.06 % Pb . . .	200	0.54	7.6	3.3	3.3
1.0 % Pb . . .		0.25	5.9	3.2	3.4
2.3 % Pb . . .		0.19	4.4	2.1	2.5
Pure selenium . .		0.39	5.8	3.5	2.8
Alloys—					
0.06 % Pb . . .	210	0.61	7.3	4.4	3.9
2.3 % Pb . . .		0.44	6.2	3.5	3.8
Pure selenium . .		0.70	7.8	4.7	3.4
Alloys—					
0.06 % Pb . . .	215	0.13	2.4	1.6	1.8
1.0 % Pb . . .		0.16	2.6	2.1	1.9
2.3 % Pb . . .		0.17	2.7	1.9	1.9
Pure selenium . .		0.21	3.3	2.2	2.1

(3) *Substances increasing the Dark Resistance and Light Ratios.*

Tables IV., V. and VI. show the effect of increasing concentrations of thallium, bismuth, and copper; the effect is marked. The effect was so marked with 5 per cent. thallium, 12 per cent. thallium and 20 per cent. thallium that the cells behaved as insulators.

TABLE IV.—SELENIUM-THALLIUM. (40 mins. annealing.)

	Annealing Temperature (°C.).	Median Dark Resistance (megohms).	Median Values in White Light (100 lux).		
			Instantaneous Light Ratio.	Terminal Light Ratio.	Decay Light Ratio.
Alloys—					
0.005 % Tl . . .	180	6.9	24.5	7.1	4.6
0.025 % Tl . . .		18.8	35.0	8.5	6.1
0.05 % Tl . . .		7.1	26.0	6.7	5.0
0.25 % Tl . . .		∞	—	—	—
0.5 % Tl . . .		∞	—	—	—
Pure selenium . .		28.5	43.5	10.5	6.1

TABLE IV.—SELENIUM-THALLIUM. (40 mins. annealing.)—Continued.

	Annealing Temperature (°C.).	Median Dark Resistance (megohms.)	Median Values in White Light (100 lux).		
			Instantaneous Light Ratio.	Terminal Light Ratio.	Decay Light Ratio.
Alloys—					
0.005 % Tl . . .	190	0.32	7.2	3.2	2.9
0.025 % Tl . . .		0.81	8.9	3.8	3.4
0.05 % Tl . . .		1.6	15.2	5.0	3.2
0.1 % Tl . . .		13.5	34.5	7.5	5.7
0.25 % Tl . . .		23.0	20.3	9.1	6.1
0.5 % Tl . . .		81.5	39.5	13.2	6.5
Pure selenium . . .		0.26	4.8	2.7	2.5
Alloys—					
0.005 % Tl . . .	200	0.48	8.9	4.6	3.1
0.025 % Tl . . .		0.63	10.5	8.7	3.4
0.05 % Tl . . .		1.5	16.0	8.9	3.0
0.1 % Tl . . .		5.1	41.0	21.0	3.9
0.25 % Tl . . .		50.0	50.0	27.0	5.4
0.5 % Tl . . .		31.0	46.0	30.0	5.7
Pure selenium . . .		0.28	4.7	2.9	2.9
Alloys—					
0.005 % Tl . . .	210	0.30	5.4	3.3	3.0
0.025 % Tl . . .		0.30	4.4	2.7	2.7
0.05 % Tl . . .		0.20	3.1	2.2	2.2
0.1 % Tl . . .		0.26	5.1	3.5	2.5
0.25 % Tl . . .		1.8	12.8	6.2	4.1
0.5 % Tl . . .		3.7	13.4	7.8	4.1
Pure selenium . . .		0.12	2.8	2.0	1.9
Alloys—					
0.005 % Tl . . .	215	0.59	4.8	4.3	2.5
0.025 % Tl . . .		0.36	3.9	3.0	2.5
0.05 % Tl . . .		0.08	2.7	1.3	1.8
0.1 % Tl . . .		0.60	5.2	3.5	2.6
0.25 % Tl . . .		0.52	4.4	3.5	2.6
0.5 % Tl . . .		2.1	5.9	4.1	3.4
Pure selenium . . .		0.77	5.2	4.4	3.0

TABLE V.—SELENIUM-BISMUTH. (40 mins. annealing.)

	Annealing Temperature (°C.).	Median Dark Resistance (megohms).	Median Values in White Light (100 lux).		
			Instantaneous Light Ratio	Terminal Light Ratio.	Decay Light Ratio.
Alloys—					
0.08 % Bi . . .	180	16.4	38.0	9.8	5.0
0.28 % Bi . . .		46.0	58.0	9.0	6.5
2.25 % Bi . . .		25.0	41.0	8.8	6.3
4.64 % Bi . . .		50.0	35.0	11.0	4.6
Pure selenium . . .		8.5	24.1	8.2	4.4
Alloys—					
0.008 % Bi . . .	190	6.3	20.0	7.0	3.8
0.28 % Bi . . .		5.4	25.0	7.8	4.3
2.25 % Bi . . .		11.4	21.0	6.5	3.6
4.64 % Bi . . .		16.7	21.0	6.5	3.6
Pure selenium . . .		1.2	11.8	5.1	3.3

TABLE V.—SELENIUM-BISMUTH. (40 mins. annealing.)—*Continued.*

	Annealing Temperature (°C.).	Median Dark Resistance (megohms).	Median Values in White Light (100 lux.)		
			Instantaneous Light Ratio.	Terminal Light Ratio.	Decay Light Ratio.
Alloys—					
0.08 % Bi . .	200	0.4	7.0	4.5	
0.28 % Bi . .		0.5	8.2	5.4	
2.25 % Bi . .		1.1	4.0	6.2	
4.64 % Bi . .		12.5	5.0	3.5	
Pure selenium .		0.63	8.3	4.5	2.9
Alloys—					
0.08 % Bi . .	205	0.93	7.5	6.8	
0.28 % Bi . .		1.4	12.0	9.9	
2.25 % Bi . .		2.2	5.3	4.6	
4.64 % Bi . .		1.45	4.5	3.8	
Pure selenium .		0.55	6.0	4.2	2.7
Alloys—					
0.08 % Bi . .	210	0.7	6.9	6.2	
0.28 % Bi . .		1.9	10.2	12.8	
2.25 % Bi . .		1.4	4.2	4.1	
4.64 % Bi . .		1.1	2.1	2.6	
Pure selenium .		0.51	5.3	4.0	2.6
Alloys—					
0.08 % Bi . .	215	0.63	5.2	4.2	3.6
0.28 % Bi . .		1.3	5.6	4.0	2.9
2.25 % Bi . .		0.95	2.2	2.6	1.4
4.64 % Bi . .		2.9	5.9	4.5	1.5
Pure selenium .		0.39	5.3	3.9	2.7

TABLE VI.—SELENIUM-COPPER. (40 mins. annealing.)

	Annealing Temperature (°C.).	Median Dark Resistance (megohms).	Median Values in White Light (100 lux.)		
			Instantaneous Light Ratio.	Terminal Light Ratio.	Decay Light Ratio.
Alloys—					
0.002 % Cu . .	170	20.0	39.5	12.3	6.8
0.012 % Cu . .		73.0	34.5	9.8	5.7
0.04 % Cu . .		62.5	30.0	11.0	4.3
0.17 % Cu . .		104.0	23.5	8.9	4.9
Pure selenium .		7.2	28.0	8.0	4.8
Alloys—					
0.002 % Cu . .	180	3.7	24.5	5.5	5.0
0.012 % Cu . .		12.5	19.0	10.0	4.9
0.04 % Cu . .		15.6	33.0	10.7	5.2
0.17 % Cu . .		23.0	31.5	15.1	6.4
Pure selenium .		2.6	16.3	5.8	3.9
Alloys—					
0.002 % Cu . .	190	2.0	16.7	5.1	4.7
0.012 % Cu . .		4.9	20.8	10.0	4.3
0.04 % Cu . .		6.8	23.8	14.3	4.0
0.17 % Cu . .		16.4	30.5	17.7	5.1
Pure selenium .		1.2	14.7	5.9	3.8

TABLE VI.—SELENIUM-COPPER. (40 mins. annealing.)—*Continued.*

	Annealing Temperature (°C.).	Median Dark Resistance (megohms).	Median Values in White Light (100 lux).		
			Instantaneous Light Ratio.	Terminal Light Ratio.	Decay Light Ratio.
Alloys—					
0.002 % Cu .	200	0.24	3.8	2.3	2.3
0.012 % Cu .		1.8	8.3	5.7	3.0
0.04 % Cu .		0.89	8.7	4.9	3.3
0.17 % Cu .		0.85	7.9	4.6	3.8
Pure selenium		0.20	5.3	2.8	2.3
Alloys—					
0.002 % Cu .	210	0.30	3.9	3.4	2.6
0.04 % Cu .		0.52	4.3	3.7	2.5
0.17 % Cu .		0.53	5.8	3.7	3.3
Pure selenium		0.15	3.3	2.6	1.7
Alloys—					
0.002 % Cu .	215	0.30	2.3	2.0	2.3
0.012 % Cu .		1.7	6.4	6.8	2.7
0.04 % Cu .		0.87	6.9	4.2	3.2
0.17 % Cu .		1.0	7.3	5.3	3.3
Pure selenium		0.24	3.8	3.1	2.2

Similar results were obtained with mercury and silver; small percentages of silver had a very marked effect in increasing the resistance of the light sensitive film.

General Conclusions.

It appears that the result of adding small quantities of foreign bodies to the selenium film and subsequently annealing it, thus rendering it light sensitive, is to produce phenomena which are analogous to those observed in the study of homogeneous and heterogeneous catalysis. Some substances depress the resistance and light sensitivity of the light sensitive film, some are indifferent, while others have a marked effect in increasing the resistance and the light sensitivity. Iron had the effect of decreasing the Dark Resistance and the Light Ratios; zinc and lead were indifferent; while thallium, bismuth, copper, mercury and silver had the effect of increasing the Dark Resistance and the Light Ratios, at the same annealing temperature. In general, the relation existing between the Light Ratios and the Dark Resistance of the light sensitive film is very similar to that existing with pure selenium. The Light Ratios are higher at the lower annealing temperatures, and in addition, when foreign substances depressed or increased the Dark Resistance so also did they depress or increase the Light Ratios, at constant temperature of annealing.

The interpretation of this result appears to be that the addition of any of the substances mentioned does not in general increase the median value of the Light Ratios for a given Resistance to a higher value than would correspond to that of a pure selenium film with the same Dark Resistance. Such additions, however, may produce considerable dis-

tortion in the form of the curve obtained by plotting annealing temperature against the Resistance or the Light Ratios of the light sensitive film. This being the case, the conclusion is that these foreign bodies play little part in assisting or retarding the ejection and recombination of electrons under the influence of the impinging light, but they do play an important part in determining the chemical constitution of the crystalline light sensitive mass at any one annealing temperature. These experiments have all been carried out shortly after the preparation of the cell under identical conditions in order that the measurements should be obtained at the time when any catalytic effect that might be caused by the added foreign substances would be expected to be most in evidence.

REVIEW OF BOOK.

Numerical Examples in Physics. By W. N. BOND, M.A., D.Sc., Lecturer in Physics in the University of Reading. (London: Edward Arnold & Co. 1931. 18 x 11 cms. Pp. vi + 128. Price 4s.).

This small book consists of 450 short stories many of which are so very problematical that still shorter explanatory solutions are provided at the end. They are classified as 'First year,' 'Intermediate' Pass, General Honours or Part I. Tripos, Special Honours or Part II. Tripos, from which it will appear that preparation for success in examinations is one of the aims kept in view. The reader is, however, warned that 'facility in performing numerical calculations should not be confused with a full knowledge of physics,' and some of the questions appear not to have been set and possibly will never be set at examinations. Hence this must not be regarded as a mere cram book, but as an aid to the training of a physical student in his subject. Emphasis is laid on the necessity of stating numerical results to just as many significant figures as the data justify and other hints are given which are unfortunately often omitted from similar collections.

It is easy to omit data which are essential to a problem. Thus in Ex. 53 if the water is collected in a tank at ground level the answer is different from that required if it runs away on reaching the ground. In strictness this question is correctly worded, but a student always needs to picture the precise circumstances that are intended by the examiner.

In Ex. 57 it would be more correct to replace 'a downward force of g per unit mass' by 'a downward force per unit mass equal to g '. Ex. 58 will puzzle a student to decide whether the stone will not also experience an air retardation as well as the falling drop, and he will be quite right to hesitate in deciding; especially if Ex. 39 on the curling-stone happens to be set in the same paper. The calculation of the surface tension of a sessile drop of pitch which has taken some years to form may have very questionable value in view of the fact that a tuning fork may be made from pitch: the force of surface tension being very small. (Ex. 94.)

Ex. 166 is rather simple as a 'General Honours' question when the latent heat is taken as independent of temperature.

These are only a few points which occur to a reader on first glancing through the book and they are mainly from the early part.

In reality the collection as a whole is an exceedingly valuable one and will prove very useful both to teachers and students. The hints given at the end are also of the right sort.

PHYSICAL PROPERTIES OF MIXTURES OF ACETONE AND BROMOFORM.

BY VIOLET CORONA GWYNNE TREW.

Received 16th February, 1932.

A reference to the literature dealing with physical properties of binary mixtures of organic liquids shows that while considerable work has been done on mixtures of acetone and chloroform, very few physical properties have been determined for mixtures of acetone and bromoform. Qualitative determination shows that a considerable heat change results on mixing acetone and bromoform.

The following investigation was carried out to determine if similar deviations from the mixture law occurred to those obtained by previous investigation for mixtures of acetone and chloroform. The following represent the results obtained for the properties; density (D_4^{25}), heat change on mixing, specific heat, viscosity and refractive index, for a series of mixtures of acetone and bromoform.

Experimental.

Preparation of Mixtures.—The purest specimens of acetone and bromoform obtainable were procured and were both submitted to further purification, by careful drying and fractional distillation until a constant boiling fraction was obtained. The density was then determined as a further test of purity, the following values being obtained.

$$\begin{array}{ll} \text{Acetone} & D_4^{25} = 0.7847. \\ \text{Bromoform} & D_4^{25} = 2.8794. \end{array}$$

Throughout the experiments the bromoform was kept in the dark and as far as possible out of contact with the air in order to prevent decomposition.

A series of nine mixtures was then made up by starting with pure acetone at one end and adding increasing amounts of bromoform. A series was thus obtained having the approximate compositions of 10, 20, 30, moles per cent. of bromoform and ending with pure bromoform. The mixtures were made up by adding the approximate calculated volume of bromoform from a burette to a known volume of acetone to give the required composition, and the exact composition was then determined by weight, weighings being taken to the nearest 0.1 milligram. The liquids were weighed in a small flask, by difference, so that the small buoyancy correction involved could be neglected, as being almost the same for all weighings. The mixtures were then sealed in small glass flasks of the exact capacity of the contained liquid and kept in the dark until required for the experiments.

Table I. Column 2 gives the actual compositions in moles per cent. of bromoform in the mixtures used.

TABLE I.—ACETONE-BROMOFORM MIXTURES.

Mixture.	Composition in Moles. Per Cent. Bromoform.	Experimental Density D_4^{25}	Density Percentage Deviation.	Viscosity (η^{25}) Experimental Value. ($\times 10^3$).	Viscosity Percentage Deviation.
Acetone	0	0.7847	0	3.05	0
I.	9.69	1.024	3.65	4.07	11.33
II.	20.14	1.270	4.98	5.29	15.36
IIIa.	27.27	1.438	6.05	—	—
III.	33.20	—	—	6.96	16.35
IV.	42.80	1.784	6.13	8.47	14.02
V.	49.52	1.931	5.98	9.54	12.64
VI.	59.74	2.127	4.47	11.31	9.88
VII.	67.66	2.283	3.68	12.68	8.12
VIII.	79.97	2.507	1.95	15.03	4.63
IX.	91.66	2.720	0.59	17.30	1.76
Bromoform	100	2.879	0	18.94	0

Determination of Density.—The density of the pure liquids and of the mixtures was determined at 25° C. A small pycnometer of 2 c.c. capacity was used, and the density calculated from the mean of three determinations. The theoretical value of the density had the Mixture Law been obeyed was calculated, and hence the deviation in density was determined by difference.

Table I. shows in column 3 the observed density values, and in column 4 the calculated percentage deviation.

If a curve of deviation against composition is plotted, it will be seen that the maximum deviation occurs between the 30 and 50 moles per cent. composition, a deviation of as much as 6 per cent. being obtained here.

Viscosity.—The viscosity coefficient was determined for each of the pure substances and for the mixtures, using a form of the Poiseuille viscosimeter as modified by Ostwald. The viscosimeter was chosen of such dimensions that the minimum time of flow taken by any of the liquids used was not less than 60 seconds, so that from the dimensions of the viscosimeter used, Reynolds' criterion $v < 1000 \eta/\eta d$ for non-turbulent flow was well satisfied. All determinations were carried out at 25° C.

The viscosity of the pure liquids and the mixtures was calculated from the mean of three determinations differing by not more than $\frac{1}{4}$ second from each other, using the formula $\eta_1 = \frac{d_1 t_1}{dt} \times 8.91 \times 10^{-3}$

where η_1 = viscosity coefficient of the liquid, d_1 its density and t_1 the time of flow, and d and t represent the density and time of flow for water using the value 8.91×10^{-3} for the viscosity of water.

Table I. shows the experimental values in column 5. Column 6 represents percentage deviations from the theoretical values that should be obtained if the Mixture Law were obeyed, calculated from the viscosity of the pure constituents. On plotting the deviations a maximum deviation of about 16 per cent. is obtained at just over 30 moles per cent. composition.

Refractive Index.—The refractive index of the mixtures and the constituents was determined at 25° by means of a Pulfrich refractometer, using sodium light. The angle of refraction was taken in all cases from the mean of three determinations differing from each other by not more than one minute of arc.

Table II. shows the experimental refractive index in column 2, while column 3 gives the percentage deviation. Here a maximum deviation is given at the 50 moles per cent. composition, the deviation being about 0.8 per cent. at this point.

TABLE II.—ACETONE BROMOFORM.

Mixture.	Refractive Index Experimental.	Refractive Index Percentage Deviation.	Sp. Refractivity.	Mol. Refractivity.
Acetone	1.35657	0	.2794	16.21
I.	1.38342	0.275	.2280	17.54
II.	1.41143	0.491	.1994	19.40
III A.	1.43046	0.619	.1798	19.99
IV.	1.46887	0.720	.1563	22.08
V.	1.48558	0.760	.1487	22.98
VI.	1.50838	0.647	.1401	24.43
VII.	1.52637	0.588	.1344	25.52
VIII.	1.55251	0.368	.1274	27.23
IX.	1.57705	0.146	.1219	28.82
Bromoform	1.59445	0	.1179	29.80

From the refractive index values the specific and molecular refractivities were calculated using the Lorentz and Lorenz formulæ

$$r = \frac{\mu^2 - 1}{\mu^2 + 2} \cdot \frac{1}{d},$$

and

$$R = \frac{\mu^2 - 1}{\mu^2 + 2} \cdot \frac{m}{d},$$

where r is the specific and R the molecular refractivity, μ the refractive index, d the density and m the molecular weight. In the case of the mixtures a mean molecular weight was calculated from the proportions of each constituent present.

Table II. columns 4 and 5 show the values obtained for these. On plotting the specific refractivity against the percentage composition in grams per cent. a straight line was obtained, and similarly on plotting the molecular refractivity against the composition in moles per cent. only a very slight positive deviation was obtained, the curve being very slightly above the straight line joining the two pure constituents.

The straight line obtained on plotting the specific and molecular refractivities against composition in grams and moles per cent. respectively does not indicate that the mixture is ideal for these properties. If the refractive index and density, calculated from the Mixture Law,

for each mixture are substituted in the equation $r = \frac{\mu^2 - 1}{\mu^2 + 2} \cdot \frac{1}{d}$ and the

results obtained plotted against compositions in grams per cent, a curve is obtained lying slightly above the straight line joining the pure constituents. Hence the experimentally obtained straight line represents an actual deviation. That this deviation is not merely due to the density

deviation may be shown by using the theoretical refractive index and experimental density values in the above equation when again a curve results slightly below the straight line. Hence the experimental deviation is an actual, though small, deviation in refractive index.

Heat of Mixing.—The heat change, on mixing, was determined by the usual calorimetric method, using a silver-plated copper calorimeter. All readings were corrected for radiation. The usual precautions, *i.e.* use of double-walled thermal vessels, etc., were taken to prevent loss of heat by cooling during the experiments. The heat change on mixing was calculated from the equation

$$H = \frac{c(m_1 + m_2)\left(t_3 - \frac{t_1 + t_2}{2}\right) + w(t_3 - t_1)}{m_1 + m_2},$$

where H = heat change, in calories, c specific heat of the mixture, m_1 and m_2 the weights of the two constituents, t_3 the final temperature at the time of mixing, t_1 and t_2 the two initial temperatures and w the water equivalent of the calorimeter and thermometer.

The specific heat for each mixture, required in this calculation, was determined by the method of mixtures, using a known weight of pure silver heated to 60° C.

Table III. shows in column 2 the specific heat of each of the first set of mixtures. Column 3 gives the compositions of the mixtures used for the heat change on mixing, while column 4 shows the values of the quantity of heat evolved in calories per gram for each mixture.

TABLE III.—ACETONE BROMOFORM.

Mixture.	Specific Heat.	Composition for Heat of Mixing Only. Per Cent. Bromo- form in Moles.	Specific Heat for Heat of Mixing Calculation. (From Specific Heat Curve.)	Heat of Mixing in Calories Per Gram.
Acetone	.513	0	—	0
I.	.402	9.01	.406	1.06
II.	.323	20.68	.320	1.93
III.	.257	29.96	.271	2.27
IIIb.	—	37.15	.244	2.32
IV.	.225	—	—	—
V.	.216	49.52	.208	2.40
VI.	.182	59.48	.183	1.99
VII.	.169	67.45	.168	1.60
VIII.	.145	80.04	.150	1.09
IX.	.132	92.87	.131	0.55
Bromoform	.128	100	—	0

Theoretical.

From a consideration of the results obtained, it is evident that mixtures of acetone and bromoform show marked deviations from the Mixture Law. In the case of every property investigated a deviation was obtained. Even in the case of the refractive index a maximum deviation of nearly 0.8 per cent. was obtained.

This result is similar to those of Zawidski ¹ and Hubbard ² who found

¹ Zawidski, *Z. physik. Chem.*, **35**, 129, 1900.

² Hubbard, *Z. physik. Chem.*, **74**, 207, 1910.

for mixtures of acetone and chloroform a deviation of the refractive index values from the ideal values.

Quite a number of mixtures of organic liquids have been shown to give considerable deviations for some properties and yet exhibit none in the case of the refractive index. The deviation obtained in the case of this pair of liquids, as in the case of acetone and chloroform, indicates that some very marked change takes place on mixing the two liquids. It has been suggested that in the case of acetone and chloroform there are two types of change going on. (1) A formation of a compound between one molecule of acetone and one of chloroform, when these are

mixed in the solution giving a compound of the type

$$\begin{array}{c} \text{Me} \quad \text{OH} \\ \diagdown \quad \diagup \\ \text{C} \\ \diagup \quad \diagdown \\ \text{Me} \quad \text{C} (\text{Cl}_3) \end{array}$$

or (2) A gradual deassociation of the originally associated acetone molecules as these are more and more diluted by the addition of chloroform.

The experimental results obtained in the investigation would indicate the same two tendencies at work in the case of mixtures of acetone and bromoform.

The deviations are in general somewhat larger than those for mixtures of acetone and chloroform, which would be expected from the greater divergence in density and molecular weight of the molecules of the two constituents. If the changes that take place on mixing were solely due to compound formation (one molecule + one molecule) the percentage deviation curves should be symmetrical about the 50 moles per cent. axis. That this is not the case can be seen on plotting the results, when, for all properties, a decided bias to the right of this line is obtained, mixtures containing less than 50 moles per cent. bromoform showing a higher deviation than corresponding mixtures on the other side of the 50 moles per cent. line. This bias might be explained as due to the formation of a co-ordination compound containing the acetone and bromoform in proportions, other than equimolecular. The fact that a well-defined maximum is not obtained at the same point for all properties makes this appear unlikely. This shift to the side of the 100 per cent. acetone concentration is explainable by considering that the acetone molecules which are known to be associated³ undergo de-association on adding the bromoform.

Thus the mixtures containing the least bromoform have actually a greater proportion of unassociated molecules. The deviation curves therefore show a bias to the acetone end. In addition, then, to the probable formation of a compound the deviations indicate that the properties of the mixture are influenced by at least one other factor, probably a gradual deassociation of the acetone.

The heat of mixing and density deviation curves show maxima at the same point, while the viscosity deviation curve gives one at a smaller, and the refractive index at a greater percentage of bromoform. The fact that the maximum deviation does not occur at the same point for every property appears to indicate that the factors causing deviation are considerably complex, some properties being more influenced than others. This would be expected as some properties are more truly molecular than others.

³ Beckmann, *Z. physikal. Chem.*, **2**, 715, 1888.

Summary.

1. The density, viscosity, refractive index, heat of mixing and specific heat of a series of mixtures containing varying proportions of acetone and bromoform have been determined.

2. In all cases deviations from the mixture law that should govern the behaviour of ideal mixtures are obtained.

3. Such deviations are similar to those obtained by other investigators for mixtures of acetone and chloroform.

4. It seems probable that, as in the case of mixtures of acetone and chloroform, the deviations are due to molecular-compound formation between the two constituents, modified by other factors such as deassociation of the one constituent in the presence of the other.

The author desires to express her thanks to Professor J. F. Spencer for his advice and interest during the course of this research, and to the Council of the Chemical Society for a grant from the Research Fund toward the cost of materials.

*Laboratory for Physical Chemistry,
Bedford College for Women,
London.*

ON VARIATIONS OF INTER-ATOMIC DISTANCES WITH THE CHANGE FROM THE CUBIC FACE- CENTERED ARRANGEMENT TO THE CUBIC BODY-CENTERED OR TO THE HEXAGONAL CLOSE-PACKED ARRANGEMENT.

BY DR. H. PERLITZ.

Received 16th February, 1932.

1. Professor V. M. Goldschmidt has pointed out that the inter-atomic distances between neighbouring atoms in crystals depend on the type of co-ordination, *i.e.* upon the arrangement and number of the neighbouring atoms.¹ He has shown that a decrease in the co-ordination number is accompanied by a decrease of inter-atomic distance.² In particular he states that the decrease of inter-atomic distances on changing from the cubic face-centered arrangement (co-ordination number 12) to the cubic body-centered arrangement (co-ordination number 8) is equal to about 3 per cent.,³ and that the variation of inter-atomic distances should be practically or absolutely zero,⁴ or at any rate less than 1 per cent.,⁵ on changing from the cubic close-packed arrangement (co-ordination number 12) to the hexagonal close-packed arrangement (co-ordination number 12). Professor Goldschmidt deduces his figures for inter-atomic distances with the change of the type of co-ordination by comparing the inter-atomic distances in suitably chosen binary compounds in which

¹ *Z. physikal. Chem.*, 1928, **133**, 399; *Trans. Faraday Soc.*, 1929, **25**, 262, 280.

² *Ibid.*, **25**, 263, 280.

³ *Z. physikal. Chem.*, 1928, **133**, 415; *Trans. Faraday Soc.*, 1929, **25**, 281.

⁴ *Z. physikal. Chem.*, 1928, **133**, 414-416.

⁵ *Skrifter Norske Videnskaps-Akademi*, 1926, **1**, 2, 47.

the atoms are in comparable states. This means that in order to obtain the necessary data he brings about the different types of co-ordination by chemical substitution of the atoms. Therefore, the values for variations of inter-atomic distances calculated by Professor Goldschmidt represent the joint effect of a modification of the geometry and of an alteration of the nature of the neighbouring atom. Values for variations of inter-atomic distances which are not affected by an alteration in the nature of the neighbouring atom, but which take into account solely the modification of the geometry cannot be deduced from these data. They may, however, be deduced from variations of inter-atomic distances which accompany polymorphic transitions, since in this case variations in inter-atomic distances are due only to changes in the types of co-ordination. Data of this kind are collected in Tables I. and II. and are illustrated in Figs. 1 and 2.

TABLE I.

Substance.	Decrease of Inter-atomic Distances in Per Cent.	Based on :—
Fe . .	2.5	Lattice constants in the A_1 -point. ⁶
Cu-Zn .	2.5	Lattice constants in the region of transition from the face- to the body-centred arrangement. ⁷
Ag-Cd .	2.5	
Fe-Co .	2.4	
Fe-Ni .	2.2	
	2.1	
Fe-Mn .	2.4	Lattice constants for co-existing face- and body-centred arrangements. ⁸
Cu-Mn-Al	2.1	
Cu-Mn-Al	1.3	
C-steel .	2.6	
Ni-steel .	2.8	
	2.0	Volumes per atom at both boundaries of the region of transition from the face- to the body-centered arrangement as deduced by extrapolation. ⁹
	1.8	
	1.9	
NiCr-steel	2.1	
CrNi-steel	2.2	
Cu-Zn .	2.3	Volumes per atom at both boundaries of the region of transition from the face- to the body-centered arrangement as deduced by extrapolation. ⁹
Ag-Zn .	3.3	
Ni-Al .	2.1	

2. Table I. and part of Fig. 1 refer to the change from the cubic face-centered arrangement to the cubic body-centered arrangement.

⁶ A. Westgren and G. Phragmén, *Z. physikal. Chem.*, 1922, 102, 8.

⁷ E. A. Owen and G. D. Preston, *Proc. Phys. Soc.*, 1923, 36, 60 (Cu-Zn); H. Åstrand and A. Westgren, *Z. anorg. Chem.*, 1928, 175, 92 (Ag-Cd); A. Ōsawa, *Sci. Rep. Tôhoku Univ.*, 1930, 19, 119 (Fe-Co); L. W. McKeehan, *Physic. Rev.*, 1923, 21, 405; and A. Ōsawa, *Sci. Rep. Tôhoku Univ.*, 1926, 15, 388 (Fe-Ni); E. Ohman, *Z. physikal. Chem.*, 1930, 88, 96 (Fe-Mn); E. Persson, *Z. Physik*, 1929, 57, 121 (Cu-Mn-Al).

⁸ J. F. T. Young, *Phil. Mag.*, 1923, 46, 300 (Cu-Mn-Al); A. Westgren and G. Phragmén, *Z. physikal. Chem.*, 1922, 102, 13 (C-steel); A. Westgren and A. E. Lindh, *Z. physikal. Chem.*, 1921, 98, 203-205, and F. Wever, *Mitt. Kaiser-Wilhelm-Inst. Eisenforschung*, 1921, 3, 55 and 54, and F. Kirchner, *Ann. Physik*, 1922, 69, 76 (Ni-steel); F. Wever, *Mitt. Kaiser-Wilhelm-Inst. Eisenforschung*, 1921, 3, 54 and 55 (NiCr- and CrNi-steel).

⁹ A. Westgren and A. Almin, *Z. physikal. Chem.*, 1929, 85, 20 and 24 (Cu-Zn, Ag-Zn and Ni-Al).

As may be seen, the variations of inter-atomic distance lie between— 3·3 and — 1·3 per cent., with the arithmetical mean at about — 2½ per cent. It may therefore be concluded that, on the changing from the cubic face-centered arrangement to the cubic body-centered arrangement,

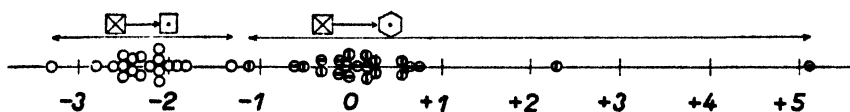


FIG. 1.—Distribution of the variations of inter-atomic distances. The 19 marks ○ show the distribution of variations of inter-atomic distances on changing from the cubic face-centered arrangement to the cubic body-centered arrangement for Ag-Zn; Ni-steel; C-steel; Cu-Zn, Fe, Ag-Cd; Fe-Co, Fe-Mn; Cu-Zn, CrNi-steel; Fe-Ni; Cu-Mn-Al, Ni-Al, Fe-Ni, NiCr-steel; Ni-steel; Ni-steel; Ni-steel; Cu-Mn-Al. The 11 marks □ and ○ display the distribution of variations of inter-atomic distances with the change from the cubic face-centered arrangement to the hexagonal close-packed arrangement outside and within the equatorial plane for Ag-Al; Pb-Bi; Co-Ni; Fe-Co, Fe-Co; Au-Sn, Au-Hg; Co-Ni; Co, Co; Ag-Sb; Ag-Sb, Ag-Sn, Au-Hg; Ce, Ag Sn, Au-Sn, Pb-Bi; Ag-Al; Ce; Cu-Sb; Sn-Sb.

TABLE II.

Substance.	Variations of Nearest Inter-atomic Distances in Per Cent. for Atoms.		Axial Ratios of the Hexagonal Lattice.	Based on Lattice Constants:—
	Within the Equatorial Plane.	Outside the Equatorial Plane.		
Ce .	+ 0·8	+ 0·3	1·62	For co-existing cubic and hexagonal close-packed arrangements. ¹⁰
Co .	0·0	0·0	1·633	
Fe-Co .	— 0·3	— 0·3	1·631	In the vicinities of the region of transition from the cubic to the hexagonal close-packed arrangement. ¹¹
Co-Ni .	— 0·2	— 0·2	1·632	
Co-Ni .	— 0·03	— 0·5	1·621	At the boundaries of the region of transition from the cubic to the hexagonal close-packed arrangement. ¹²
Ag-As .	+ 0·2	+ 0·2	1·633	
Ag-Sb .	+ 0·1	+ 0·2	1·634	
Cu-Sb .	+ 5·1	+ 2·3	1·572	In the region of transition from the cubic to the hexagonal close-packed arrangement. ¹³
Ag-Al .	+ 0·7	— 1·1	1·588	
Ag-Sn .	+ 0·2	+ 0·3	1·634	
Au-Hg .	— 0·1	+ 0·2	1·638	
Au-Sn .	— 0·1	+ 0·6	1·649	
Pb-Bi .	— 0·6	+ 0·6	1·66	

¹⁰ A. W. Hull, *Physic. Rev.*, 1921, 18, 89; and 1921, 17, 577-578.

¹¹ A. Osawa, *Sci. Rep. Tôhoku Univ.*, 1930, 19, 119-120 (Fe-Co); and 1930, 19, 112-113 (Co-Ni).

¹² A. Westgren, G. Hägg and S. Erikson, *Z. physikal. Chem.*, 1929, B4, 463 (Ag-Sb); S. J. Broderick and W. F. Ehret, *J. physical Chem.*, 1931, 35, 3323-3325 (Ag-As).

¹³ E. V. Howells and W. Morris-Jones, *Phil. Mag.*, 1930, 9, 995 (Cu-Sb); A. F. Westgren and A. J. Bradley, *Phil. Mag.*, 1928, 6, 282, 287 (Ag-Al); O. Nial, A. Almin and A. Westgren, *Z. physikal. Chem.*, 1931, B14, 88 (Ag-Sn); A. Pabst, *Z. physikal. Chem.*, B3, 1929, 450 (Au-Hg); Sten Stenbeck and A. Westgren, *Z. physikal. Chem.*, 1929, B14, 94-95 (Au-Sn); A. Solomon and W. Jones, *Phil. Mag.*, 1931, 11, 1093 (Pb-Bi).

the inter-atomic distance decreases by about $2\frac{1}{2}$ per cent. The left-hand side of Fig. 1 shows further that, out of the nineteen values for transitions from the face-centered to the body-centered arrangement, sixteen form a compact cluster, outside which lie only three values. The three non-conforming data are: -3.3 for Ag-Zn, -2.8 for one of the Ni-steel samples, and -1.3 for one of the Cu-Mn-Al samples. These values are, however, the least dependable ones, the value for Ag-Zn being deduced by extrapolation over a relatively long distance; the sample of Cu-Mn-Al is a specimen the previous history of which is unknown; the value 2.8 for the sample of Ni-steel is not in accord with the data for three other samples of Ni-steel, which are 1.8 , 1.9 and 2.0 . It seems, therefore, permissible to disregard the three non-conforming data, *i.e.* to conclude that the variations of inter-atomic distances lie between -2.8 and -1.8 per cent. with the arithmetical mean at about $-2\frac{1}{2}$ per cent. We may therefore reassert that *on changing from the cubic face-centered arrangement to the cubic body-centered arrangement the inter-*

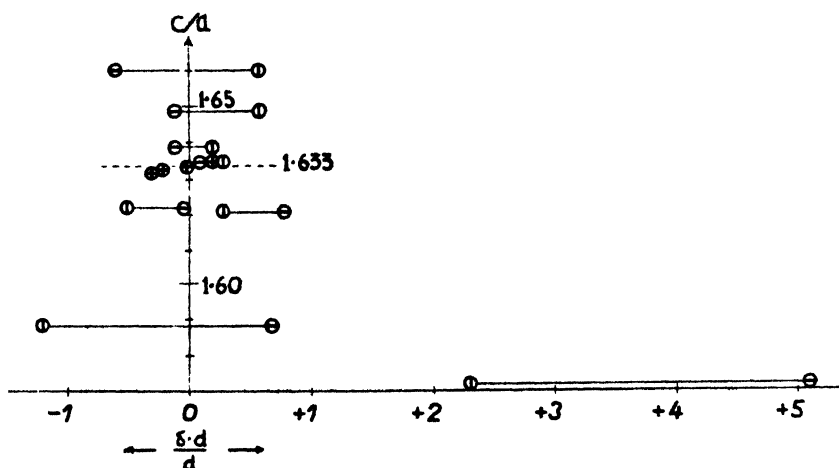


FIG. 2.—The variations of inter-atomic distances $\delta d/d$ within (\otimes) and outside (\odot) the equatorial plane, plotted against the axial ratios c/a of the hexagonal lattices to show that the variations tend to approach zero with the axial ratio approaching 1.633 .

atomic distance decreases by about $2\frac{1}{2}$ per cent., i.e. a little less than the corresponding decrease deduced by Professor Goldschmidt.

3. Table II., part of Fig. 1, and Fig. 2 refer to the change from the cubic close-packed arrangement to the hexagonal close-packed arrangement. As may be seen, the variations of inter-atomic distance lie between -1.1 and $+5.1$ per cent., with the arithmetical means at about $+0.5$ and $+0.2$ per cent. for variations respectively outside and within the equatorial plane. Comparing the right-hand side of Fig. 1 with its left-hand side we see that the data for the eleven substances plotted on the right-hand side cover thrice the range covered by the data for the thirteen substances plotted on the left-hand side. This large difference in the variation of inter-atomic distances on changing from the cubic close-packed to the hexagonal close-packed arrangement is connected with the axial ratios of the hexagonal lattices, as may be seen from Fig. 2 in which variations of inter-atomic distances are plotted against axial ratios. From Fig. 2 we conclude that the variations in the

inter-atomic distances for directions within and outside the equatorial plane decrease to zero with the axial ratio approaching 1.633, the value corresponding to the packing of spheres. It may therefore be stated that *with the change from the cubic close-packed arrangement to the hexagonal close-packed arrangement the variations of inter-atomic distances depend upon the axial ratio of the hexagonal lattice and the variation is zero for the axial ratio 1.633.* This statement contains as a special case Professor V. M. Goldschmidt's assumption with regard to the variation of inter-atomic distances on changing from the cubic to the hexagonal close-packed arrangement.

Summary.

(1) From an examination of the data for inter-atomic distances of thirteen substances at the transition from the cubic face-centered to the cubic body-centered arrangement, it is concluded that this kind of polymorphic transition leads to a decrease of inter-atomic distances by about two and a quarter per cent.

(2) From an examination of the data for inter-atomic distances of eleven substances at the transition from the cubic close-packed arrangement to the hexagonal close-packed arrangement, it is concluded that in this type of polymorphic transition the variation of inter-atomic distances depends on the axial ratio of the hexagonal lattice, and that the variation of inter-atomic distances decreases to zero with the axial ratio approaching 1.633.

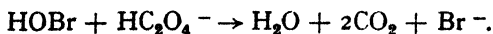
*The University,
Tartu, Esthonia.*

THE KINETICS OF THE OXIDATION OF OXALIC ACID BY CHLORINE.

BY ROBERT OWEN GRIFFITH AND ANDREW McKEOWN.

Received 24th February, 1932.

In a recent paper¹ it has been shown that the rate of reaction between bromine and oxalates, acid oxalates, or oxalic acid is determined by the process



The object of the present communication is to demonstrate that the reaction between chlorine and oxalic acid has an analogous mechanism, and thus that the process is essentially one between HOCl (formed by hydrolysis of the chlorine) and the HC_2O_4^- ion. For various reasons, it has not been possible for us to make as extended a study of the chlorine as of the bromine reaction. In the first place, the oxidation of oxalic acid by chlorine is, under comparable conditions, much faster than the oxidation by bromine, and indeed conveniently measurable speeds are attainable only in the presence of considerable concentrations of the strongly retarding agents hydrochloric acid and chlorides. This in effect limits the study of the reaction to acid solutions of moderate and high ionic strength. Again, the high degree of volatility of chlorine

¹ Griffith, McKeown and Winn, *Trans. Far. Soc.*, **28**, 107, 1932.

from its aqueous solutions renders accurate kinetic data rather difficult of attainment. Finally, a complete survey of the reaction entails the application of certain equilibrium and activity data which are at present only partially available. We have, therefore, confined ourselves to carrying out a sufficient number of kinetic measurements to demonstrate the applicability of the aforementioned mechanism of reaction.

The only previous kinetic measurements of this reaction which we have found in the literature are a few made by Bhattacharya and Dhar,² who do not, however, discuss the reaction mechanism.

Experimental.

Chlorine was prepared by the action of HCl on KMnO_4 , and a nearly saturated solution in water was used as stock. The oxalic acid and potassium chloride employed were Kahlbaum preparations. In order to reduce errors due to volatilisation of chlorine during the measurements, the reaction mixture was contained in a suitably light-shielded 500 c.c. (or 1000 c.c.) graduated flask (hence with quite a small volume of gaseous phase above the liquid), and the course of reaction was followed by pipetting out small (5 or 10 c.c.) samples from the body of the liquid. Blank experiments showed this procedure to be unattended by serious losses in chlorine. The sample was run into potassium iodide solution and an excess of solid sodium bicarbonate added, followed by excess of standard sodium arsenite solution. By back titration with a standard iodine solution the chlorine content of the sample was determined. Experiments have been carried out at 10°, 15° and 20° C. in the presence of HCl (0.25 — 0.7 *N*) and of mixtures of HCl and KCl. The initial concentration of chlorine was usually about $M/100$ to $M/150$ while that of oxalic acid was varied between $M/80$ and $M/20$.

Reaction Kinetics and Experimental Results.

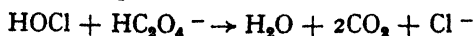
The results of the kinetic experiments are summarised in Table I. The sixth column of this table gives the *initial* values of the unimolecular constant with respect to total titratable chlorine. This k_{uni} falls regularly throughout each run concomitantly with the decreasing oxalic acid content, but its initial value may always be taken as a rough measure of rate of reaction at constant chlorine content. Comparison of these values of k_{uni} shows that:

(a) the rate of reaction is, *cet. par.*, roughly proportional to the concentration of oxalic acid (*cf.* experiments 5 and 6 or 10 and 11);

(b) with constant $[\text{H}_2\text{C}_2\text{O}_4]$ and constant $[\text{H}^+]$, the velocity is roughly inversely proportional to $[\text{Cl}^-]$;

(c) with constant $[\text{H}_2\text{C}_2\text{O}_4]$ and constant $[\text{Cl}^-]$, the velocity is nearly inversely proportional to the square of $[\text{H}^+]$.

These results are quantitatively accounted for by the assumption that the rate-determining reaction is



The retardation by chloride ion is thus attributed to its effect on the hydrolysis of the chlorine, the much greater retardation by H^+ ion to its similar effect on this hydrolysis added to its effect on the first stage of ionisation of the oxalic acid.

² Bhattacharya and Dhar, *J. Chim. physique*, **26**, 556, 1929.

We therefore write for the rate of reaction

$$\frac{dx}{dt} = k[\text{HOCl}][\text{HC}_2\text{O}_4^-] = kK \frac{[\text{Cl}_2][\text{HC}_2\text{O}_4^-]}{[\text{Cl}^-][\text{H}^+]},$$

where K is the hydrolytic constant of chlorine, and $[\text{Cl}_2]$ is the concentration of *free* chlorine in solution. The remainder of the titratable chlorine is present as Cl_3^- (the concentration of HOCl being never greater in any of our experiments than 1 per cent. of the total chlorine). Writing $K_3 = [\text{Cl}_2][\text{Cl}^-]/[\text{Cl}_3^-]$ and the total titratable chlorine $= a - x$, it follows that

$$[\text{Cl}_2] = \frac{K_3}{K_3 + [\text{Cl}^-]} \cdot (a - x).$$

Since in any given experiment the variations of $[\text{H}^+]$ and $[\text{Cl}^-]$ with x are small, it is sufficiently accurate to use mean values $[\text{H}^+]_m$ and $[\text{Cl}^-]_m$ in the kinetic equation. Accordingly

$$\frac{dx}{dt} = kK \cdot \frac{K_3}{K_3 + [\text{Cl}^-]_m} \cdot \frac{[\text{HC}_2\text{O}_4^-]}{[\text{H}^+]_m} \cdot (a - x).$$

$[\text{HC}_2\text{O}_4^-]$ can now be expressed as a linear function of x as shown in our previous paper,³ and the above equation is then integrated to give kK . The values of kK thus computed are given in the last column of Table I.

TABLE I.

Expt. No.	$[\text{H}_2\text{C}_2\text{O}_4]_{\text{init.}}$	$[\text{HCl}]$	$[\text{KCl}]$	μ	Init. $k_{\text{uni.}} \cdot 10^3$	kK
<i>t</i> = 10° C.						
1	<i>M</i> /40	0.378	—	0.383	0.290	0.112
2	<i>M</i> /40	0.504	—	0.508	0.137	0.114
<i>t</i> = 15° C.						
3	<i>M</i> /40	0.255	—	0.260	1.78	0.220
4	<i>M</i> /40	0.255	—	0.260	1.70	0.216
5	<i>M</i> /40	0.255	—	0.260	1.72	0.216
6	<i>M</i> /80	0.252	—	0.254	0.887	0.217
7	<i>M</i> /40	0.3825	—	0.387	0.580	0.225
8	<i>M</i> /40	0.3825	—	0.387	0.594	0.233
9	<i>M</i> /40	0.510	—	0.513	0.272	0.234
10	<i>M</i> /40	0.510	—	0.513	0.273	0.232
11	<i>M</i> /20	0.504	—	0.511	0.581	0.227
12	<i>M</i> /40	0.252	0.25	0.508	0.985	0.242
13	<i>M</i> /40	0.252	0.25	0.508	0.968	0.241
14	<i>M</i> /40	0.252	0.50	0.758	0.673	0.254
15	<i>M</i> /40	0.252	0.75	1.008	0.464	0.255
16	<i>M</i> /40	0.1008	0.90	1.012	1.75	0.261
17	<i>M</i> /40	0.1008	1.90	2.012	0.675	0.236
<i>t</i> = 20° C.						
18	<i>M</i> /40	0.378	—	0.383	1.21	0.444
19	<i>M</i> /40	0.504	—	0.508	0.529	0.440
20	<i>M</i> /40	0.7056	—	0.708	0.204	0.457

³ Griffith, McKeown and Winn, *loc. cit.*, p. 113, case (d).

The calculations obviously involve a knowledge of K_1 the first ionisation constant of oxalic acid, and also of the constant K_3 of trichloride formation. As regards K_1 we have used the data of Dawson, Hoskins and Smith,⁴ and have assumed that the variation of K_1 with ionic strength μ is the same in HCl and in mixtures of HCl and KCl as in KCl (to which Dawson's data refer); that is, we have used the relation

$$\log_{10} K_1 = \bar{2}.756 + 0.42\sqrt{\mu} - 0.275\mu.$$

The constant K_3 probably also varies with ionic strength, but its magnitude is such that minor variations in it have no serious effect upon the value of the function $K_3/\{K_3 + [\text{Cl}^-]\}$ which occurs in the above kinetic equation. From the data of Sherrill and Izard⁵ we find $K_3 = 5.9$ at 25°, and assuming equal heats of dissociation for Cl_3^- and Br_3^- we infer that K_3 equals 5.58, 5.28 and 5.0 at 20°, 15° and 10° respectively. It should be noted that appreciable errors in these figures do not seriously affect the calculated constant kK .

The evaluation of the individual velocity coefficient k from the above data involves a knowledge of K , the hydrolytic constant of chlorine, and of its variation with μ . The values of $K(\mu = 0) = K_a$ at various temperatures have been calculated by Lewis and Randall⁶ from Jakowkin's data.⁷ These are $K_a \times 10^4 = 2.58, 3.28$, and 4.06 at 10°, 15°, and 20° respectively. Variation of K with ionic strength is, as we have previously shown,⁸ expressed by $K_a = K \cdot \gamma_{\text{H}^+} \cdot \gamma_{\text{Cl}^-}$, where γ = activity coefficient. The value of the product $\gamma_{\text{H}^+} \cdot \gamma_{\text{Cl}^-}$ may be derived for

TABLE II.

Expt. No.	μ	kK	$\gamma_{\text{H}^+} \cdot \gamma_{\text{Cl}^-}$	$K \cdot 10^4$	k
$t = 10^\circ \text{C.}$					
1	0.383	0.112	0.569	4.54	246
2	0.508	0.114	0.574	4.50	254
$t = 15^\circ \text{C.}$					
3, 4, 5, 6	0.259	0.217	0.578	5.68	382
7, 8	0.387	0.229	0.569	5.77	397
9, 10, 11	0.513	0.231	0.574	5.72	404
12, 13	0.508	0.241	0.533	6.16	392
14	0.758	0.254	0.526	6.24	407
15	1.008	0.255	0.526	6.24	408
16	1.012	0.261	0.508	6.46	404
17	2.012	0.236	0.605	5.42	435
$t = 20^\circ \text{C.}$					
18	0.383	0.444	0.569	7.14	622
19	0.508	0.440	0.574	7.07	622
20	0.708	0.457	0.599	6.78	674

⁴ Dawson, Hoskins and Smith, *J.C.S.*, 1884, 1929.

⁵ Sherrill and Izard, *J. Amer. Chem. Soc.*, **53**, 1667, 1931.

⁶ Lewis and Randall, *Thermodynamics*, p. 508.

⁷ Jakowkin, *Z. physik. Chem.*, **20**, 613, 1899.

⁸ Griffith, McKeown and Winn, *loc. cit.*, p. 123, equation (30).

HCl solutions from the data of Randall and Young,⁹ and for mixtures of HCl and KCl from the data of Harned.¹⁰ Applying these we obtain the results given in Table II. The units of the bimolecular velocity constant k in the last column are litres/moles-minutes.

Discussion of Results.

The approximate constancy of the values of k at each temperature is to be regarded as strong support for the mechanism adopted. There appears to be a slight rise of k with increasing ionic strength, as was found for the analogous reaction of bromine with oxalic acid, but in the present instance the accuracy of the kinetic measurements themselves and of the subsidiary data used in the calculation is insufficient to permit of a definite conclusion in this connection.

From experiments (1) and (2) at 10° and experiments (18) and (19) at 20°, the temperature coefficient of kK is found to be 3.91; that of the initial $k_{uni.}$ is about 4.0. (The latter is not in good agreement with the temperature coefficient of $k_{uni.}$, viz. 2.95, given by Battacharya and Dhar² for the temperature interval 15°–25°.) The temperature coefficient of the velocity constant k of the rate-determining process $\text{HOCl} + \text{HC}_2\text{O}_4^- \rightarrow \text{H}_2\text{O} + 2\text{CO}_2 + \text{Cl}^-$ has the value 2.49 between 10° and 20°. This figure is practically the same as the temperature coefficient (2.52) found for the reaction between HOBr and HC_2O_4^- , and corresponds to the same critical increment of about 15,000 calories. The velocity constants of the two processes are also of similar orders of magnitude. Thus at 20° k for the HOCl reaction is about 600, while k for the HOBr reaction is about 16,500.

⁹ Randall and Young, *J. Amer. Chem. Soc.*, **50**, 989, 1928.

¹⁰ Harned, *ibid.*, **48**, 326, 1926.

*Muspratt Laboratory of Physical and Electrochemistry,
University of Liverpool.*

THE STRUCTURE OF THIN FILMS OF CERTAIN METALLIC OXIDES.

BY PROFESSOR W. L. BRAGG, F.R.S., AND MR. J. A. DARBYSHIRE.

Received 29th February, 1932.

The structures described in this paper were examined by the method of electron diffraction. A narrow electron beam fell normally on the thin film and the diffraction pattern was recorded on a photographic plate at a distance of 24 cms. from the film. Potentials between 30,000 and 60,000 volts were used.

Apparatus.

In essential principles the apparatus corresponded to that first employed by G. P. Thomson.¹ A few special features may be briefly mentioned.

¹ G. P. Thomson, *Proc. Roy. Soc.*, **117A**, 600, 1928.

FIG. 1.

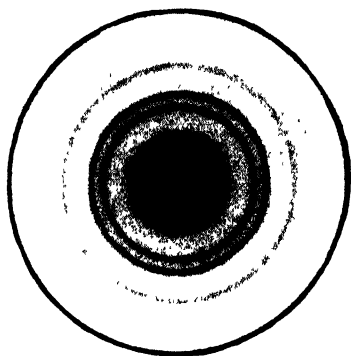


FIG. 2.

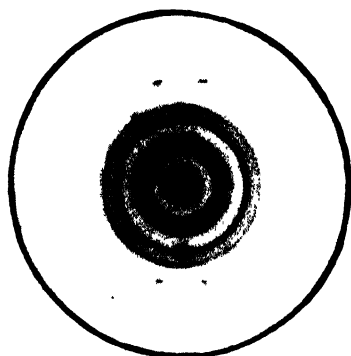
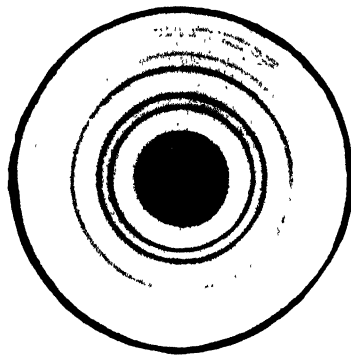


FIG. 3.

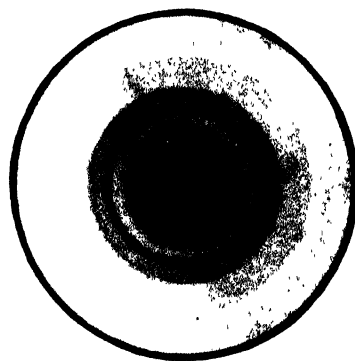


FIG. 4

PLATE 1 —Electron diffraction photographs

[To face page 523.

The electron stream was obtained from a hot cathode consisting of a tungsten spiral. The effective slit system consisted of a hole 1 mm. in diameter close to the cathode, and a final pin-hole 0.2 mm. in diameter close to the specimen which was at a distance of 24 cms. from the cathode. The distance from specimen to photographic plate was also 24 cms. The specimen was mounted on a small brass washer on a movable arm, so that it could be lowered into position in front of the beam, and adjusted for the best position, by manipulating the lever with a vacuum-tight winch. The camera accommodated a quarter plate, which could similarly be lowered into position out of a light-tight box when an exposure was to be made. When desired, the part exposed was limited by a transverse slit, and in this case a large number of exposures could be made on the same plate.

The high-tension was obtained from a motor-generator and transformer, the generator giving 50-200 volts at 500 cycles. A voltage range between 10 and 60 kV could be obtained by altering the field current of the generator. The current was rectified with an Osram E. H. T. valve, and smoothed by two Pertinax condensers in parallel, each of 0.02 mfd. It was then passed through the secondary of an induction coil, which gave further smoothing and reduced surges. The ripple was measured by a valve voltmeter such as is used for testing wireless circuits for uniform amplification over audio-frequency ranges. When the current is 1 or 2 milliamperes, the fluctuation is about 70 volts for a mean voltage of 35,000, which is sufficiently small to give an effectively constant de-Broglie wave-length.

The voltage was measured by determining the spark gap between two copper spheres 13 cm. in diameter whose distance apart could be adjusted. This was found to be a very sensitive and accurate method of estimation. The voltage as calculated by the spark gap agreed closely with that determined by measuring the diffraction rings given by a gold film.

In the case of each specimen, the diameter of some well-defined diffraction ring was measured for a series of voltages, each determined by the spark gap. The mean value of the corresponding crystal spacing was taken and used in measuring the spacings of other rings of the diffraction pattern.

Zinc Oxide.

A sample of pure zinc was melted in a clay crucible and a loop of thin copper wire was dipped into the molten metal and slowly withdrawn. A thin film of metallic zinc stretches across the loop, having a number of fine holes over its surface. Across these holes is stretched a thin transparent film, and such films were mounted in the diffraction tube. We are indebted to Professor G. P. Thomson for suggesting this method of preparation. Photographs of this material are shown in Figs. 1 and 2.

It was expected that this material would be the usual hexagonal ZnO, but measurement shows that this is not the case. The measurements of the radii of the rings, the corresponding crystal spacings, and photometer measurements of the intensities of the rings are given in Table I. The rings are not uniform in intensity around their circumference, probably due to preferred orientation of the crystalline matter, and hence the intensities can only be regarded as approximating to those which would be obtained in the ideal case of perfect random orientation of the crystalline particles.

The great majority of the rings correspond in position and approximately in intensity, with those to be expected from a cubic modification of ZnO, the unit cell being a face-centred cube of side 4.62 Å., containing 4 molecules of ZnO. The indices of the cubic lattice corresponding to each ring are given in column 5 of Table I.

TABLE I.

Ring.	Radius cms. (obs.).	Inten- sity (obs.).	d/n , Å.	Indices.	d/n , Å. for $a = 4.62$.	Intensity (calc.).	Radius (calc.).
(a) Zinc Oxide. Voltage 33,200.							
2	0.59	235	2.93	111	2.66	264	.62
3	0.66	78	2.45	200	2.31	45	.71
4	1.02	218	1.65	220	1.63	90	1.01
5, 6	1.18	190	1.37	311, 222	1.39, 1.33	61	1.19, 1.24
7	1.32	3	1.25	321	1.24	0	1.33
8	—	—	—	400	1.15	2	—
9, 10	1.57	91	1.06	331, 420	1.06, 1.03	20	1.56, 1.60
12	1.77	9	0.93	422	0.94	14	1.75
13	1.86	4	0.88	511, 333	0.89	8	1.86
14	2.00	4	0.82	440	0.82	3	2.01
15	2.13	?	0.77	531, 600	0.78, 0.77	7	2.12, 2.15
(b) Zinc Oxide. Voltage 36,000.							
1	0.39		3.98	110?	3.27		0.47
2	0.536		2.90	111	2.66		0.58
3	0.620		2.49	200	2.31		0.67
4	0.942		1.65	220	1.63		0.95
5	1.125		1.37	311	1.39		1.12
6	1.150		1.35	222	1.33		1.16
7	1.240		1.25	321?	1.24		1.25
8	miss- ing		—	400	1.15		1.34
9	1.464		1.06	331	1.06		1.46
10	1.500		1.03	420	1.03		1.50
11	1.57		0.99	332	0.98		1.58
12	1.66		0.93	422	0.94		1.65
13	1.77		0.88	511, 333	0.89		1.75
14	1.92		0.81	440	0.82		1.89
15	2.01		0.77	531, 600	0.78, 0.77		1.99, 2.02
16	2.11		0.73	620	0.73		2.12
17	2.24		0.69	533, 622	0.70		2.22
18	2.45		0.63	640	0.64		2.42
19	2.57		0.60	642	0.62		2.53

Apart from certain discrepancies, discussed below, these results are in good agreement with a cubic lattice of side 4.62 Å. The intensities, though approximate, further indicate that the structure is of the zinc blende type, the atoms of zinc and oxygen being on two-face centred lattices, with atoms of one kind at the centre of a tetrahedral group of atoms of the other kind. There seems to be little doubt that the film consists of a cubic modification of ZnO, which bears the same relation to the well-known hexagonal ZnO, as cubic zinc-blende ZnS does to hexagonal wurtzite ZnS. This is further confirmed by the dimensions

of the structure. Thus, in hexagonal ZnO the Zn-O distance is 1.97 Å., whereas in the proposed structure, with $a = 4.62$ Å., the distance Zn-O is 1.99 Å. Owing to the discrepancies mentioned above, we hesitated to draw this conclusion from the results in Table I(a), and sought to check it by obtaining a photograph with a greater number of rings. The good agreement shown in Table I(b), for such a photograph, Fig. 2 appears to establish the structure.

Nevertheless, certain discrepancies appear for which we cannot suggest an explanation. In the first place, two well-marked inner rings, 2 and 3, are not in the expected positions. The observed radii are 0.536 cm. and 0.620 cm., the calculated radii for $a = 4.62$ Å. being 0.58 cm. and 0.67 cm. These differences are much larger than can be accounted for by error of measurement. A number of plates show the same effect. The radii have been measured visually, and by photometry, and in every case the radii of the two inner rings are smaller than would be expected for a cell deduced from the radii of all the rings outside them. If the proposed structure is correct, two of the strongest rings should appear here and no others are possible in this region. The observed rings are very intense and sharp, and can hardly be other than the two in question.

It may be remarked that the diffracting power of the zinc atom falls off very quickly with increasing angle in this region, and if the diffraction maxima are formed by a small number of conspiring planes the effect of the steep decline in scattering power is to displace the maxima inwards towards the central spot. Calculation shows, however, that this consideration can only account for a fraction of the observed effect.

Another unexplained feature is the appearance of two "forbidden" rings. A ring (1) inside 111 is clearly present. It has been assigned indices 110 in the table. The observed radius is 0.39 cm., and that corresponding to 110 would be 0.47 Å., but such a displacement is in accord with the displacement of 200 and 111. Between rings (6), 222 and (9)331 there should be a ring (8) 400. This is not visible, though it appears faintly on the photometer curve, and calculation shows that it must be expected to be very weak. However, a very well-defined though faint ring appears in precisely the position expected for (7) 321. These two rings (1) and (7), cannot be accounted for by traces of metallic zinc or hexagonal ZnO, for the strongest lines of these substances do not appear in these positions.

In spite of these discrepancies, the extensive agreement throughout the table would seem to justify the conclusion that the film is formed of a cubic modification of ZnO, with the zincblende structure, and with a unit cube containing four molecules of side 4.62 Å.

One of these oxide films was heated in hydrogen at 250° C. for three hours and allowed to cool slowly in a current of the gas. This had no observable effect on the diffraction pattern, and no change in the lattice spacing could be detected, but it is necessary to mention that the specimen was *in vacuo* about three hours before the photograph was taken.

A sample of zinc oxide prepared by ignition of metallic zinc as described by Ponte² was sprinkled on to fine mesh copper gauze and photographed by transmission of the electron beam through the gauze. This gave a pattern corresponding to the usual hexagonal zinc oxide as found by Ponte, and differing entirely from that given by the previous specimen.

² M. Ponte, *Ann. Physique*, 13, 395, 1930.

Lead Oxide PbO_2 .

Lead was melted in a crucible, and a thin film withdrawn on a loop of copper wire as in the case of zinc. The sheet of metallic lead has transparent sections across which thin films of oxide are stretched. Such films are mounted as before.

The photograph, Fig. 3, has well-defined rings which correspond closely to the rings to be expected for a microcrystalline film of PbO_2 . This substance has the tetragonal rutile structure. The lattice constants, according to a recent determination by one of the authors (J.A.D.),³ using the X-ray powder method, are $a = 4.931 \text{ \AA.}$, $c = 3.367 \text{ \AA.}$ The values of d/n calculated from the rings correspond quite well with the values to be expected from such a structure. These values are given in Table II, and in cases where overlapping occurs in the electron diffraction pattern the weighted mean of the calculated values is given. These have been weighted according to their observed intensity in the X-ray powder photograph.

TABLE II.

PbO_2 . Voltage 34,800 ($\lambda = 0.65 \text{ \AA.}$).

Ring.	Radius in cms. (obs.).	$d_{hkl} \text{ \AA.}$ (obs.).	d_{hkl} (calc.).	Indices.
1	0.45	3.51	3.49	110
2	0.56	2.82	2.78	101
3	0.64	2.47	2.46	200
4	0.88	1.80	1.81	121, 220
5	1.04	1.52	1.54	130, 112
6	1.10	1.44	1.43	301, 202
7	1.28	1.23	1.24	231, 222
8	1.37	1.15	1.15	132, 330
9	1.45	1.09	1.10	240, 103
10	1.62	0.97	0.96	332, 150
11	1.70	0.93	0.92	242, 303

There appears in addition, in Fig. 3, a network of spots similar to those first obtained by Kikuchi⁴ when an electron beam traverses a thin mica sheet. More recently this effect has been investigated by G. P. Thomson⁵ and F. Kirchner.⁶ The spots are spaced in rows which make an angle of $68^\circ 20'$ with each other. Their average distance apart along the two row-directions are 0.549 cm. and 0.540 cm. respectively (Fig. 5(c)).

Such a pattern corresponds to diffraction by a two-dimensional net of scattering points. These points must be arranged on rows which include an angle of $68^\circ 20'$. The spacings of the rows correspond to the distances between the points on the photograph. They are given by the formulæ $d = \frac{24\lambda}{0.540'}$, and $d = \frac{24\lambda}{0.549'}$, and are 2.89 \AA. and 2.84 \AA. respectively. The corresponding net of points is shown in Fig. 5(b).

³ J. Chem. Soc., 211, 1932.

⁴ S. Kikuchi, *Proc. Imp. Acad. Japan*, 270, 1928.

⁵ G. P. Thomson, *Proc. Roy. Soc.*, 133A, 1, 1931.

⁶ F. Kirchner, *Z. physikal. und chem. Unterricht*, Part III, 44, 1930.

As will be clear from the figure, the diffracting net which accounts for the diffraction pattern corresponds very closely with the projection of the lead atoms in PbO_2 upon the plane (100). The lead atoms are

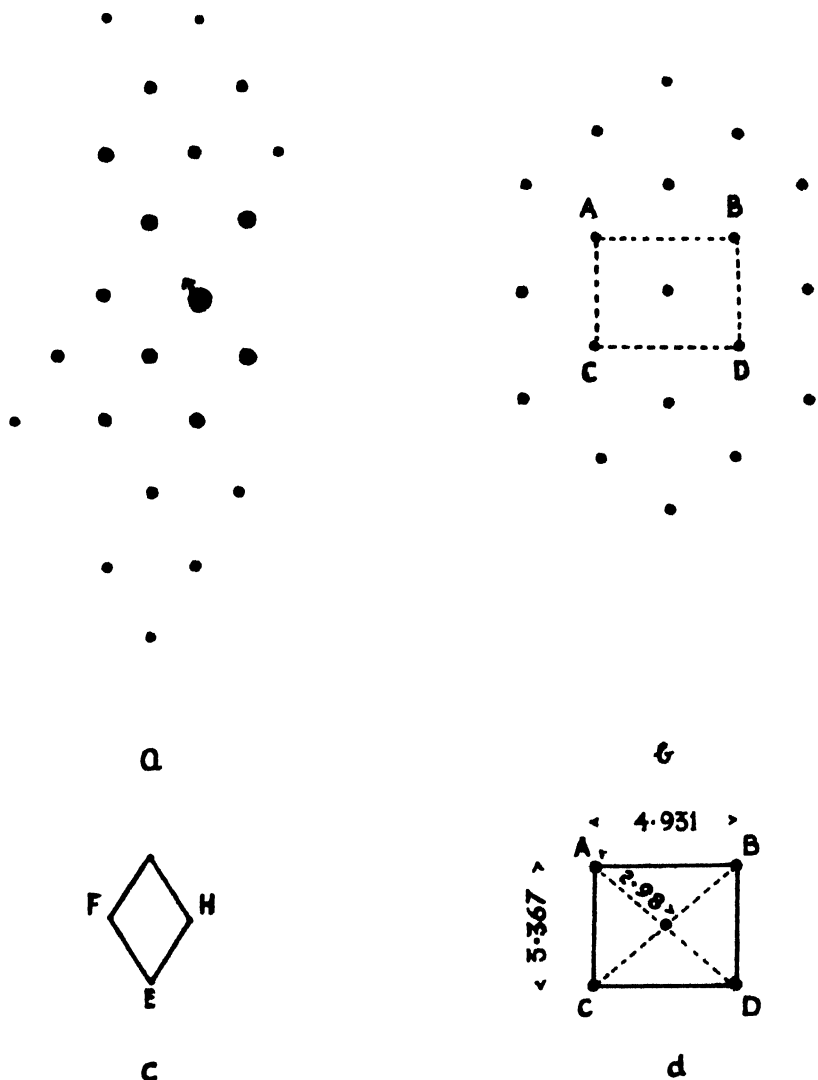


FIG. 5.

- (a) Reproduction of pattern in Fig. 3. The arrow denotes the relative position of ring centre.
 (b) Two dimensional diffracting net deduced from (a).
 (c) Scale of pattern (a). $EF = 0.540$ cm., $EH = 0.549$ cm., $\angle FEH = 68^\circ 20'$.
 (d) Projection of unit cell of PbO_2 on (100), which corresponds to (b).

at the corners and centre of the unit tetragonal cell. It appears that the pattern is formed by a small single crystal of PbO_2 , which has been fixed in the PbO_2 film, and which happens to be placed with a face (100) nearly parallel to the plane of the film. The small difference in the

spacing of the diffracted spots along the rows in either direction would be accounted for by a tilting of the crystal of PbO_2 through an angle of about 10° around an axis perpendicular to $[110]$ in Fig. 5(d).

The centre of the ring system does not coincide with the centre of the system of spots. The one is displaced from the other by about 0.06 cm., in the direction shown by the arrow in Fig. 5(a). So large a displacement can hardly be accounted for by the small single crystal being on one side of the irradiated area, for this is only 0.02 cm. in width. We cannot suggest any explanation of the displacement.

The possibility of getting single small crystals of a simple crystal like PbO_2 which give such sharp effects is interesting, because it affords a means of studying in greater detail this little understood phenomenon of the behaviour of a crystal as a two-dimensional grating.

Oxide of Tin, SnO_2 .

The specimen was prepared by oxidising a sheet of pure tin foil, 0.01 mm. in thickness, in a flame. The foil was drawn rapidly through the flame, and becomes a fine lace-work containing a number of suitable areas over which the oxide film is very thin.

The photograph is shown in Fig. 4 and the results of the measurements are shown in Table III. The spacings and intensities correspond satisfactorily with those to be expected from a film of micro-crystalline SnO_2 . The tin atoms are on a body-centred tetragonal lattice in this structure, with $a = 4.72 \text{ \AA}$, $c = 3.17 \text{ \AA}$.

TABLE III.

Oxide of Tin, Sn_2O_3 . Voltage 28,200.

Ring.	Radius.	d_{hkl} .	Indices.	Intensity (photometer).	Relative Intensity (calculated).
1	0.52	3.35	110	783	1000
2	0.68	2.56	101	437	444
3	0.78	2.23	200	250	78
4	1.02	1.71	220, 211	514	462
5	1.26	1.39	301, 311, 130	262	205
6	1.50	1.17	400, 321, 312		
7	1.68	1.04	420, 411, 213		
8	1.95	0.89	341, 501		

Summary.

In a previous paper,⁷ analyses of the films formed by oxidation of clean nickel and copper sheets have been reported. These may be summarised together with the results given in the present paper. The films of oxide which are formed upon the surface of the heated metal in each case are as follows :—

- Copper Cu_2O , cuprite.
- Nickel NiO , with rock-salt structure.
- Zinc ZnO , a new modification with the zinc-blende structure.
- Lead PbO_2 , rutile structure.
- Tin SnO_2 , „

⁷ *Trans. Faraday Soc.*, 27, 675, 1931.

No difficulty in assigning the correct structure exists except in the case of the film formed upon molten zinc. Certain abnormalities are found in the positions of the diffraction rings, of which we have been unable to find an explanation. The general agreement is so good, even in this case, that we believe the compound to be a cubic modification, hitherto unrecorded, of ZnO .

INVESTIGATION OF THE SYSTEM $\text{KCl} - \text{PbCl}_2 - \text{H}_2\text{O}$ at 25° .

BY L. J. BURRAGE.

Received 2nd March, 1932.

Some years ago an investigation was carried out by the author on equilibria¹ in the system, $\text{KCl} - \text{PbCl}_2 - \text{H}_2\text{O}$ at 25° . Since then a comprehensive study has been made of the thermodynamics of this system at the same temperature involving both E.M.F.² and vapour pressure measurements, extended over the whole concentration range. Interest has chiefly centred round the behaviour of solutions in the neighbourhood of the quadruple point — PbCl_2 (solid) : $\text{KCl} \cdot 2\text{PbCl}_2$ (solid) : solution : vapour, and as it was necessary to establish the position of the isothermal in this region as accurately as possible, a further series of solubility determinations has been undertaken.

1. Experimental.

The experimental details are identical with those described in the previous paper,¹ and the concentrations are expressed as before in gms./1000 gms. water. The complete series of data for this region is given in Table I., and expressed graphically in Fig. 1.

TABLE I.—GM./1000 GM. WATER.

KCl	PbCl_2	Previous PbCl_2 Value.
15	3.05	3.06
30	2.31	
40	2.18	
47	2.30	
52.5	2.39	
55	2.49	2.39
58	2.60	
60	2.10	
61	1.50	
76	1.35*	
108	1.41	1.38
		1.41

* This figure was obtained after 500 hours' rotation in the thermostat at 25° , whereas the previous value of 1.38 gms. was obtained after 48 hours' rotation.

The shape of the curve is interesting in view of the sudden drop in concentration of the lead chloride on passing the potassium chloride

¹ *J.C.S.*, 1703, 1926.

² *Trans. Far. Soc.*, 23, 1927.

concentration corresponding to the quadruple point. This in itself suggests the existence of unusual relations between the partial molal free energies of the different components of the solution in this region.

2. Discussion.

Considerable difficulty has been encountered in establishing the exact position of this quadruple point, and this difficulty appears to

be connected with certain anomalies noticed in the behaviour of potassium chloride solutions of these concentrations, whether containing in addition dissolved lead chloride or not. These anomalies are apparent in solubility, E.M.F., vapour pressure and viscosity measurements.

In the case of solubility, there was a large equilibrium lag. This did not occur markedly, so long as lead chloride was the solid phase, but manifested itself as soon as the compound $\text{KCl} \cdot 2\text{PbCl}_2$ made its appearance. The solid compound could remain in contact with an unsaturated solution for a long period before equilibrium was attained, and similarly the solution could remain supersaturated although in contact with solid.

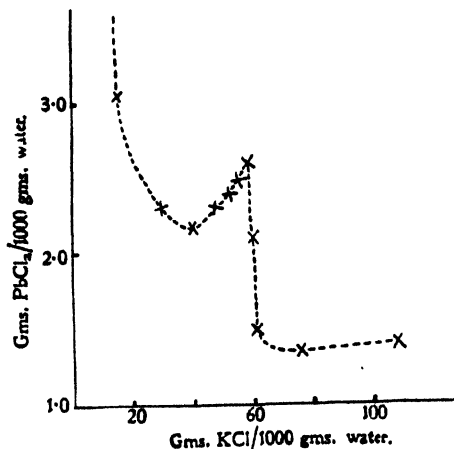


FIG. 1.

contact with an unsaturated solution for a long period before equilibrium was attained, and similarly the solution could remain supersaturated although in contact with solid.

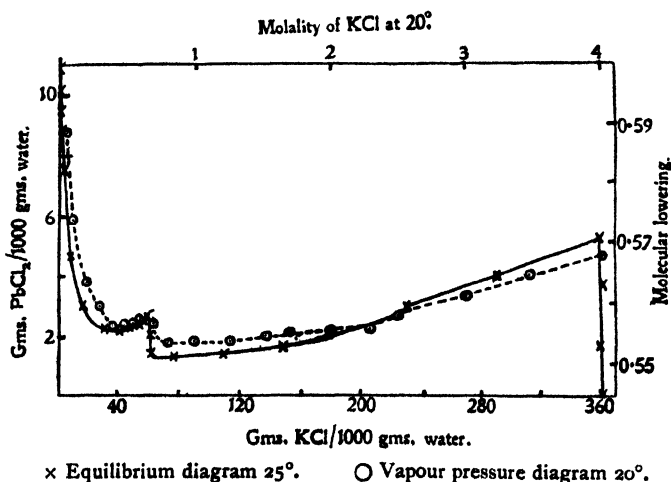


FIG. 2.

This caused a difficulty in manipulation since it had been customary to saturate at 30° and then cool to 25° , allowing the excess solid to

crystallise out. Equilibrium was more rapidly attained by this means than by approaching the solubility value from lower concentrations. A second difficulty was experienced in the coating of the lead chloride by the compound. Solid in contact with solutions in the neighbourhood of the quadruple point gave variable analytical values.

The present figure for the quadruple point is the average of a number of careful determinations and the potassium chloride value agrees well with the concentration at which the minimum occurs in the viscosity curve for pure potassium chloride solutions. (Nickels, unpublished.)

A most interesting parallel is shown in Fig. 2, where the very accurate vapour pressure figures of Lovelace, Fraser and Sease² (expressed as molecular lowering $\frac{p_0 - p_1}{M}$) for pure potassium chloride at 20° have been superimposed on the equilibrium diagram. It will be seen that there is a definite change in direction of the vapour pressure curve, corresponding to the changes in the equilibrium diagram.

No explanation of this is offered at present, as it has formed the subject of a further investigation.

Summary.

1. A detailed investigation has been carried out on the system $\text{PbCl}_2 - \text{KCl} - \text{H}_2\text{O}$ at 25°, at concentrations in the neighbourhood of the quadruple point — PbCl_2 (solid), $\text{KCl} \cdot 2\text{PbCl}_2$ (solid), vapour, and solution.

2. A parallelism has been noted between the solubility of lead chloride in potassium chloride solutions and the molecular lowering of the vapour pressure of pure potassium chloride solutions.

² *J.A.C.S.*, **43**, 102, 1921.

*King's College,
University of London.*

THE USE OF THE GLASS ELECTRODE IN TITRIMETRIC WORK AND PRECIPITATION REACTIONS. THE APPLICATION OF THE PRINCIPLE OF THE SOLUBILITY PRODUCT TO BASIC PRECIPITATES.

BY HUBERT THOMAS STANLEY BRITTON AND ROBERT ANTHONY ROBINSON.

Received 7th March, 1932.

Hughes¹ demonstrated that glass electrodes could be prepared which were sufficiently sensitive to marked changes in hydrogen-ion concentration to be used as indicators in electrometric titration. He was able to locate accurately the end-points in the titration of a solution of chromic acid and of a concentrated solution of borotartaric acid.² He also showed that it could be used to study the precipitation of basic

¹ *J. Amer. Chem. Soc.*, **44**, 2860, 1922.

² *Vide Lowry, J. Chem. Soc.*, 2857, 1929.

copper sulphate. Morton³ has since used the glass electrode to titrate a number of oxy-acids of phosphorus and solutions of bismuth, iron and copper salts in the presence of organic hydroxy-acids.

These and other workers⁴ have shown that it is possible to calibrate the E.M.F.'s of glass electrodes in terms of p_H values by employing a series of standard buffer solutions. In order to study the behaviour of certain metal-metallic oxide electrodes over a large p_H range Britton and Robinson⁵ modified the Prideaux and Prideaux-Ward Universal Buffer Solutions in such a way that the electrodes could be immersed in the solution and, by direct addition of alkali, subjected to gradual variation in p_H value between 1.8 and 12.0. Owing to the sinuous nature of the p_H curve of these buffer mixtures, the p_H values had to be determined at numerous points during the titration. Using this buffer mixture Britton and Robinson studied the antimony-antimonous oxide electrode and Britton and Dodd⁶ the tungsten electrode. The present authors⁷ have described another universal mixture which has an advantage over the Prideaux-Ward mixture in that the p_H alkali curve is an exact straight line over a wide p_H range. The present paper describes some work which was undertaken primarily to ascertain whether the glass electrode could indicate exact p_H values at any point in a titration curve, including inflexions. Hitherto this possibility has not received the attention it merits, especially when it is considered that the electrode reaction of glass is essentially heterogeneous, and therefore one which conceivably might require time before equilibrium or reproducible E.M.F.'s are established. Another point arising therefrom is how long a glass electrode is likely to adhere to its calibration potentials after being used in solutions of widely differing hydrogen-ion concentration. Moreover, we have studied its behaviour during the separation of precipitates, and in view of the conflicting p_H values which Britton,⁸ Kolthoff and Kameda,⁹ and Prytz¹⁰ have reported as prevailing during the precipitation of zinc salt solutions, these reactions have been investigated further by means of the glass electrode.

Experimental.

The glass electrode system was similar to that used by Morton,¹¹ viz. :—

Pt	$N/_{10}$ HCl quinhydrone	Glass	Test Solution	Satd. KCl or KNO ₃	N-calomel.
----	------------------------------	-------	------------------	-------------------------------------	------------

The glass electrodes, which were in the form of thin walled bulbs, were blown from a special silicate glass made by fusing silica, sodium carbonate and calcium carbonate in the proportions of 60:30:10 respectively.¹² Such glass may be procured from Messrs. Dixon of

³ *Quart. J. Pharm.*, **3**, 488, 561, 1930; **4**, 451, 1931; *Trans. Faraday Soc.*, **28**, 84, 1932.

⁴ See Britton, *Hydrogen Ions*, 2nd ed., p. 94, 1932.

⁵ *J. Chem. Soc.*, 458, 1931.

⁶ *Ibid.*, 1456, 1931.

⁷ *J. Amer. Chem. Soc.*, **53**, 832, 1931.

⁸ *J. Scientific Instruments*, **7**, 187, 1930.

⁹ Cf. Hughes, *J. Chem. Soc.*, 491, 1928; MacInnes and Dole, *J. Amer. Chem. Soc.*, **52**, 29, 1930.

¹⁰ *Ibid.*, 829, 1931.

¹¹ *Ibid.*, 127, 2124, 1925.

¹² *Z. anorg. Chem.*, **200**, 133, 1931.

Devonshire Street, W.C. 1. Little difficulty was experienced in constructing these electrodes, though it was found advantageous to blow about a dozen at a time and to select only those bulbs which, on immersion in the universal buffer solution at various stages of neutralisation, gave satisfactory galvanometer deflections.

The method of measuring the E.M.F. of the glass cell was to allow it to charge up a condenser of suitable capacity, during a definite period of time, and then to discharge the condenser suddenly through a sensitive ballistic galvanometer. This method has been used for glass electrode work by Morton and the condensers and galvanometer were supplied by the Cambridge Instrument Co. The condensers were of 0.5, 1.0, and 1.5 microfarad capacity respectively, but in practice it was found that relatively little increase in sensitivity resulted from varying the capacity within this range. The galvanometer had a coil resistance of 2986 ohms, a ballistic period of 23 secs., and a scale deflection per microcoulomb of 3100 mm. at a distance of 1 metre. The galvanometer was almost dead-beat and the throw was taken as proportional to the condenser-discharge producing it.

Efficient earthing of both the calomel electrode and the plate of the condenser, to which it was connected, was essential. The glass electrode and its connection to the condenser were insulated by passing the glass tube of the electrode through a hole in a cork, which had previously been immersed in molten paraffin wax, and then fixed in the waxed jaws of a wooden burette stand.

Owing to the high resistance of the glass electrode, very little advantage could be gained by using a variable condenser, as will be understood from the equation

$$i \times t = CE(1 - e^{-t/RC}),$$

where E is the p.d. across the glass cell, i the current, Q the charge received in t seconds by the condenser, and C its capacity. By substituting for E , 1 volt, and taking R equal to 100 megohms, it is found that the charge acquired in thirty seconds is 0.258 microcoulomb, whereas condensers of 1.5 and 0.5 microfarad capacity would receive 0.270 and 0.224 microcoulombs respectively. Thus it is seen that doubling and trebling the condenser capacity only increases the charges in the ratio of 1 : 1.15 : 1.20.

An important advantage of the cell arrangement is that at about p_H 7 the galvanometer deflection is zero, but increases on one side with diminishing p_H and on the other with increasing p_H . Provided that no asymmetry E.M.F. is set up at the glass membrane the voltage of the cell should be 0.421–0.058 p_H at 18°, so that the cell should acquire zero potential at p_H 7.3. In acid solutions the quinhydrone electrode will therefore be the positive pole, but will become the negative with solutions of p_H higher than p_H 7.3.

Calibration of Glass Electrodes.

In this work the calibration of the glass electrode system was carried out by direct titration of the modified universal buffer solution of Prideaux. A calibration curve was constructed connecting deflections with the p_H values of the electrolyte in which the glass electrode was immersed—these being accurately known for each small addition of 0.2*N* sodium hydroxide solution. Each calibration curve was exactly rectilinear from p_H 2.5 and p_H 10, so much so that if it is desired to

make p_H measurements with moderate accuracy it is only necessary to calibrate the electrode with two buffer solutions within this range, say half-neutralised acetic acid, p_H 4.73, and half-neutralised boric acid, p_H 9.20. Since, however, the whole calibration will depend on measurements at only two p_H values correspondingly greater care is necessary in determining the deflections at these two points.

Usually the electrodes have been used in solutions of p_H between 2 and 10, and for this work the calibration has not been carried beyond p_H 10. Under these conditions the electrode maintains its calibration during an ordinary day's run, but it is necessary to calibrate each day, and in very accurate work both before and after a series of titrations.

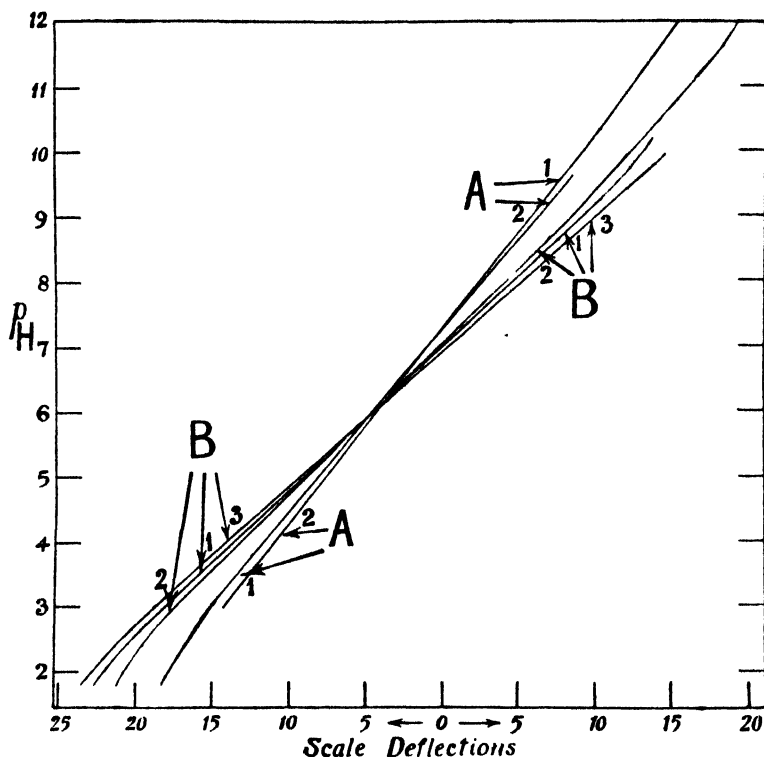


FIG. 1.

If, on the other hand, the electrode is used in very alkaline solutions it is advisable to calibrate it immediately afterwards, as the electrode is apt to lose its calibration. A series of typical calibration curves of two electrodes is shown in Fig. 1. These curves refer to two electrodes A and B, each of which was calibrated on successive days. Both are rectilinear over the major portion of the titration, *i.e.* between p_H values of approximately 2.5 and 10. Calibrations A2 and B2 were carried considerably beyond $p_H = 10$, and both show a deviation from linearity. The daily variation of these calibration curves shows no trend in any one direction; though there is a tendency for the graphs to oscillate round a point in the vicinity of the neutral point. For this reason

the electrode requires only occasional calibration if it is used in the determination of p_H values in the neutral zone.

No difficulty has been experienced in obtaining constancy in the readings, and equilibrium is apparently attained almost instantaneously, except in solutions of p_H values below 1.5, where a small drift in the potential is observed but which disappears in about five minutes, and after changing the p_H of the solution by several units as in the titration of hydrochloric acid with sodium hydroxide.

Determination of the Dissociation Constants of Weak Acids.

In order to test the ability of the glass electrode to give correct p_H values, a series of acids, and in some cases the alkali salts, have been titrated with the aid of the glass electrode at 18° and the p_H values indicated on the addition of each successive one-eighth equivalent of titrant have been used to calculate the p_K values. Table I. is a typical example of the neutralisation of a weak acid and of the variations found in the calculated p_K values. Not only do the p_K values of hydrocyanic acid reveal a remarkable degree of agreement among themselves, but the mean p_K value, 9.32, is in excellent accord with the value, $p_K = 9.35$, which Britton and Robinson⁵ obtained colorimetrically and the value

TABLE I.—TITRATION OF 100 C.C. OF 0.04*M* KCN WITH 0.2*N* HCL.

Equivs. HCl . .	0.125	0.25	0.375	0.5	0.625	0.75	0.875	Mean
p_H . .	10.15	9.79	9.53	9.34	9.11	8.87	8.48	—
p_K . .	9.30	9.31	9.31	9.34	9.33	9.35	9.33	9.32

p_K , 9.31, found by Britton and Dodd¹³ using the vapour pressure method devised by Harman and Worley.¹⁴ In the second column of Table II. are summarised the mean p_K values corresponding to a number of titration curves. Each titration was carried out on 100 c.c. of solution with 0.2*N* sodium hydroxide solution, or 0.2*N* hydrochloric acid solution in the case of the back-titration of alkali salts. In all cases excellent agreement was obtained between the p_K values calculated at intervals during the titration, the maximum deviation from the mean being ± 0.05 p_H . They are compared with the values recently found by (i) Britton and Robinson⁵ using the antimony electrode, (ii) Britton and Dodd⁶ with the aid of tungsten electrodes, and (iii) previous workers using different recognised methods.

The p_K values obtained for the first four acids in Table II. are seen to be in agreement with the accepted values. The p_K values derived for the unsaturated acids, maleic and fumaric, agree with those obtained with the antimony electrode; previous estimates of both p_{K_1} values are discordant, but the values now obtained are probably correct and find support in the determinations of Kortwright¹⁵ and Reyer.¹⁶ The value obtained for chromic acid, 6.47, is in good agreement with the hitherto unconfirmed figure of 6.40, obtained by Britton¹⁷ by means

¹³ *J. Chem. Soc.*, 2332, 1931.

¹⁵ *Amer. Chem. J.*, 18, 365, 1896.

¹⁷ *J. Chem. Soc.*, 125, 1572, 1924.

¹⁴ *Trans. Faraday Soc.*, 20, 502, 1924.

¹⁶ *Diss. Brunswick*, 1923.

536 USE OF GLASS ELECTRODE IN TITRIMETRIC WORK

TABLE II.—COMPARISON OF p_K VALUES OF ACIDS OBTAINED BY MEANS OF THE GLASS ELECTRODE WITH PREVIOUS VALUES.

Solution Titrated.	p_K			Previous Determinations.
	Glass Electrode.	Antimony Electrode.	Tungsten Electrode.	
0.04 <i>N</i> acetic acid	4.76	4.58	4.65	4.73
0.04 <i>N</i> boric acid	9.20	9.13	9.04	9.20
0.04 <i>M</i> malonic acid	p_{K_1} 2.77	2.99	—	2.70, 2.74
	p_{K_2} 5.44	5.38	—	5.36, 5.39
0.04 <i>M</i> phosphoric acid	p_{K_1} 2.00	2.01	2.00	2.03, 1.96
	p_{K_2} 6.93	6.92	7.11	6.85, 6.71
	p_{K_3} 11.75	11.85	11.73	11.57, 11.55, 12.44
0.04 <i>M</i> potassium cyanide	9.32	9.60	10.20	9.35, 9.31
0.04 <i>M</i> maleic acid	p_{K_1} 2.02	2.05	2.05	1.34, 1.94
	p_{K_2} 6.06	6.06	6.32	6.29, 5.96
0.015 <i>M</i> fumaric acid	p_{K_1} 3.00	2.98	—	2.55, 2.99
	p_{K_2} 4.35	4.40	—	4.32, 4.49
0.04 <i>M</i> sodium azide	4.77	4.97	5.18	4.59, 4.74, 5.10
0.04 <i>M</i> potassium chromate	6.47	7.07	—	6.40
0.04 <i>M</i> sodium sulphite	p_{K_1} 1.78	—	—	1.73
	p_{K_2} 6.99	7.74	8.91	7.00
0.04 <i>M</i> selenious acid	p_{K_1} 2.54	—	—	2.31, 2.40, 2.46
	p_{K_2} 8.02	8.34	—	8.05
0.04 <i>M</i> telluric acid	p_{K_1} 7.68	7.84	7.35	—
	p_{K_2} 11.19	12.5	—	—

of the hydrogen electrode. This titration also demonstrated that in the first stage of dissociation, chromic acid is a "strong" acid. The constants obtained for selenious acid compare well with those found by German.¹⁸

Titration with the glass electrode showed that selenic acid, like sulphuric, is "strong" in both stages of dissociation. In marked contrast with selenic acid, telluric acid is characterised by extreme weakness. The titration curve confirms its dibasicity corresponding to the formula H_2TeO_4 . The approximate value of 12.5 given by the antimony electrode for p_{K_2} is now seen to be too high; nevertheless the more accurate determination with the glass electrode offers no support for the hexabasic nature of telluric acid demanded by the formula, H_6TeO_6 , of Rosenheim and Weinheber,¹⁹ and Gutbier.²⁰

Behaviour of Glass Electrodes in Unbuffered Solutions.

Hitherto it has been demonstrated that the glass electrode is capable of giving accurate p_H values, but it will be understood from Tables I. and II. that all the p_H values involved in the calculation of the p_K values corresponded to solutions that were well buffered.

When it is remembered that the electrode reaction occurring at the glass-solution interface is one involving an equilibrium between sodium silicate and silicic acid, it will be realised that not only may the glass electrode itself affect the p_H of unbuffered solutions but the electrodic

¹⁸ *J. Chem. Soc.*, 470, 1931.

¹⁹ *Z. anorg. Chem.*, 69, 261, 1911.

²⁰ *Ibid.*, 29, 29, 1901.

reaction may be so interfered with that there is every possibility of the glass electrode failing to give the true p_H values of the solutions. If this view is correct, then it would be expected that the glass electrode would not indicate satisfactory p_H values during those stages of titrations when sharp changes in hydrogen-ion concentration were taking place. To test this, titrations of hydrochloric acid and phosphoric acid solutions with alkali have been followed with both the glass electrode and the hydrogen electrode. The hydrogen electrode was assumed to give the true p_H values and the differences between them and the values indicated by the calibrated glass electrode after each addition of alkali were found. Such differences are plotted in the central part of Fig. 2, and the tie-lines to the glass electrode curves of hydrochloric acid with alkali and phosphoric acid with sodium hydroxide indicate the parts of the titrations in which these errors occur. It will be seen that no errors arise in the p_H measurements of solutions which by the addition of alkali suffered small changes in hydrogen-ion concentration, wherever these changes occurred. Considerable variations, however, occurred when the titrant produced sudden changes in p_H . Thus in curve I the glass electrode p_H values were accurate until the acid was 98 per cent. neutralised, when there occurred a rapid diminution in hydrogen-ion concentration. At 99.3 per cent. the glass electrode was 0.31 p_H unit too high, whilst at 99.9 per cent. the error had become as high as 0.84 p_H unit. At complete neutralisation it was 1.6 p_H unit. Very soon after neutralisation the glass electrode indicated low p_H values between 8 and 9. As soon as the sharp increase in p_H was passed the glass electrode again indicated correct p_H values. As would be expected, similar divergences, though not so great, were noticed in the phosphoric acid titration.

Morton²¹ titrated phosphoric acid with the glass electrode, but obtained lower p_K values, *viz.*, $p_{K_1} = 1.61$, $p_{K_2} = 6.62$, $p_{K_3} = 11.25$. From these values he concluded that the two equivalence points should occur at p_H 4.1 and p_H 8.9 (observed p_H 4.0 and p_H 8.8 respectively). The first conclusion is erroneous as the expression $p_H = \frac{1}{2}(p_{K_1} + p_{K_2})$ does not hold where one stage of the neutralisation is that of a fairly strong acid, as is the case with phosphoric acid.²²

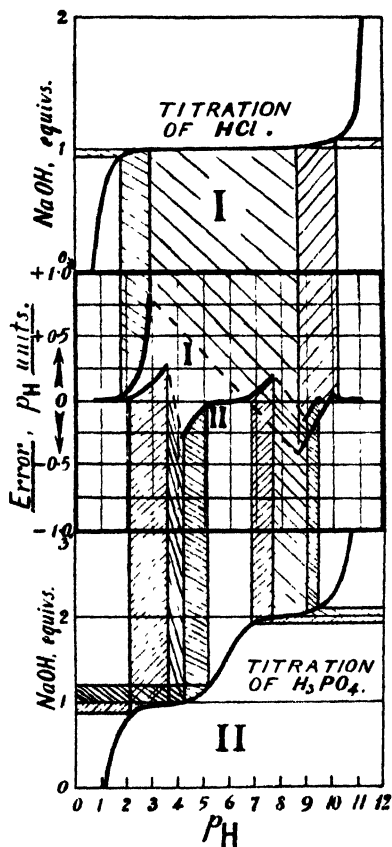


FIG. 2.

²¹ *Quart. J. Pharm.*, **3**, 438, 1930.²² See for example, Britton, *J. Chem. Soc.*, **127**, 1896, 1925.

Behaviour of the Glass Electrode in the Presence of Precipitates.

This section comprises a critical study of typical precipitations, *viz.* silver hydroxide, magnesium hydroxide and aluminium hydroxide. For obvious reasons, the hydrogen electrode is not applicable to solutions of silver salts, and Britton,²³ observed that whilst the oxygen electrode could be used to detect considerable changes in hydron concentration occurring in the reactions of silver salts, it was of little use in the estimation of the correct p_H values. Britton and Dodd⁶ made similar observa-

tions with both the antimony and tungsten electrodes. On the contrary, the solubility product of silver hydroxide is known with some degree of certainty, and as silver salt solutions are among the very few that yield pure hydroxide precipitates on treatment with alkali, it was considered that calculations of the solubility product from the p_H values established on the addition of varying amounts of sodium hydroxide to a silver nitrate solution would provide a means of ascertaining whether the glass electrode was indicating correct p_H values. The data corresponding to two titrations of silver nitrate with sodium hydroxide at 16°

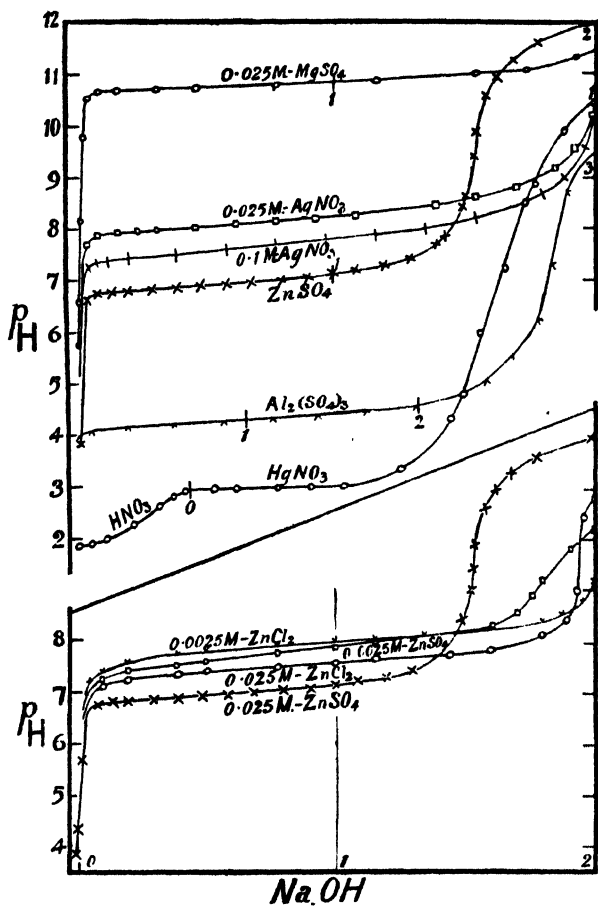


FIG. 3.

are given in Table III and the p_H curves are plotted in Fig. 3. The incidence of the inflexions with the stoichiometrical amounts of alkali shows that silver hydroxide was precipitated. The solubility product, L , was calculated from the relationship, $p_{OH} = p_{K_w} + p_H$, and the concentration, C , of silver nitrate in the solution, this being taken as equal to the silver ion concentration. In computing the value of the corrected solubility product, L_c , the silver ion concentrations were

TABLE III.—PRECIPITATION OF SILVER HYDROXIDE FROM SILVER NITRATE SOLUTION.

Equiv. NaOH.	0.1.	0.2.	0.3.	0.4.	0.5.	0.6.	0.7.	0.8.	0.9.
1. 100 c.c. 0.100M AgNO ₃ with 0.2N NaOH.									
p_H	7.48	7.54	7.61	7.69	7.81	7.92	8.03	8.21	8.56
$L \times 10^8$	1.62	1.58	1.55	1.55	1.62	1.62	1.51	1.45	1.58
$L_c \times 10^8$	1.34	1.32	1.32	1.32	1.43	1.46	1.38	1.34	1.50
2. 100 c.c. 0.025M AgNO ₃ with 0.2N NaOH.									
p_H	7.97	8.04	8.11	8.17	8.25	8.34	8.49	8.70	9.04
$L \times 10^8$	1.32	1.35	1.38	1.33	1.30	1.29	1.34	1.44	1.58
$L_c \times 10^8$	1.19	1.22	1.26	1.22	1.21	1.20	1.26	1.37	1.52

considered as being equal to α_c . The appropriate values of α were found from the conductivity data of Kohlrausch and Steinwehr.²⁴ It might perhaps be considered a more satisfactory procedure to express the solubility product, $[Ag^+][OH^-]$, in terms of "activities," thus $a_{Ag} \cdot a_{OH} = \gamma_{Ag} \cdot [Ag^+] \cdot \gamma_{OH} \cdot [OH^-] = \gamma_{Ag} \cdot [Ag^+] K_w / a_H$. Since the glass electrode depends for its calibration on a hydrogen electrode titration of a universal buffer mixture, and consequently if it can be assumed that the liquid junction potentials are eliminated by the use of a saturated potassium nitrate salt-bridge, the values given by both the hydrogen and glass electrodes are, strictly speaking, hydrogen-ion activities rather than hydrogen-ion concentrations. Moreover, as during the entire precipitation process the total ionic concentration remained constant there occurred but little variation in the activity coefficient of the silver ion. According to Lewis and Randall²⁵ its value in *N*/10 solution is 0.732 and in *N*/40 solution 0.840. Applying these factors to the mean solubility products given in Table III, values of 1.14×10^{-8} and 1.13×10^{-8} respectively are obtained.

A number of determinations of the solubility product have been made by conductivity, silver electrode and analytical methods. Table IV

TABLE IV.

$[Ag^+][OH^-] \times 10^8$	Observer.	Method.	Temp.	<i>E.</i>
0.9	Abegg and Cox	Silver electrode	25°	1.201
1.33	Present authors	Glass electrode	16°	1.211
1.50	Britton	Silver electrode	20°	1.213
1.52	Böttger	Conductivity	20°	1.213
1.93	Böttger	Conductivity	25°	1.215
2.25	Noyes and Kohr	Equilibria	25°	1.218
2.2-3.4	Whitby	Analysis	20°	1.223-1.233
3.0-5.1	Noyes and Kohr	Analysis	25°	1.226-1.240

²⁴ *Sitzber., Berl. Akad.*, 581, 1902.²⁵ *Thermodynamics*, p. 362, 1923.

summarises the more reliable data and also gives the values of the potential of the $O_2 | - | H_2$ cell calculated from the solubility of silver oxide according to the method of Lewis,²⁶ assuming the potential of the cell $O_2 | NaOH, Ag_2O | Ag$ to be 0.049 volt.

These values fall into two groups—those derived from direct analysis of the saturated solution of silver hydroxide leading to a value of the potential of the oxygen-hydrogen cell of approximately 1.230, and those derived from electrometric or conductivity methods which lead to a value²⁷ of approximately 1.212 volt. The values of $[Ag^+][OH^-]$ corresponding to the titration of silver nitrate with alkali are in accord with those deduced by other physico-chemical methods.

The behaviour of the glass electrode in the presence of precipitates may also be examined by a direct comparison between glass and hydrogen electrode titrations of suitable salts with alkali. Typical precipitation curves, *viz.*, of magnesium and aluminium sulphate solutions, are shown in Fig. 3, and the p_H data are given in Table V. (The cross-bars on the curves refer to the number of equivalents of alkali added per gram-molecule of salt, precipitation being theoretically complete at a point represented by the right axis of the graph.) Comparison of the p_H values obtained with the glass electrode and those indicated by the hydrogen electrode during the precipitation of the magnesium sulphate solution reveals that there was a tendency for the former electrode to give slightly higher values. When, however, it is remembered that precipitation occurs above p_H 10.5, which happens to be the point at which the glass electrode calibration curve begins to diverge from the straight line and the electrodic reaction is likely to be influenced by the presence of alkali metal ions in solution, the agreement appears to be all that can be legitimately expected. Although no parallel hydrogen electrode data are recorded in Table V in the case of the aluminium sulphate titration, it will be seen by comparison with the curves obtained by Britton²⁸ that the glass electrode reproduces the p_H data that would be given by the hydrogen electrode.

Fig. 3 also shows the p_H values which were observed during the titration of a solution of 0.0168*N* HNO_3 + 0.05705*N* $HgNO_3$ with alkali. The neutralisation of the free acid, during which slight precipitation occurred, is marked by a break in the curve. The precipitate which appeared thereafter was black, but on standing became green. Along with the change in colour there was a drift in the p_H values and consequently the curve in Fig. 3 is only to be taken as an approximation. It shows, however, that precipitation occurs in the vicinity of $p_H = 3.0$.

Alkali Precipitations from Zinc Salt Solutions.

Using the hydrogen electrode Britton⁸ found that basic zinc sulphate began to precipitate from a 0.025*M* solution of zinc sulphate at p_H 5.2, and was completely precipitated when 1.53 equivalents of sodium hydroxide had been added. Various workers have questioned the behaviour of the hydrogen electrode in the presence of zinc ions, and recently Kolthoff and Kameda⁹ claimed to have prepared hydrogen electrodes, covered with bright crystalline platinum, which yielded quite accurate p_H values during alkali titrations of zinc salts. These

²⁶ *J. Amer. Chem. Soc.*, **28**, 158, 1906.

²⁷ See Noyes, *J. Amer. Chem. Soc.*, **24**, 1141, 1902.

²⁸ *J. Chem. Soc.*, 127, 2121, 1925; 422, 1927.

TABLE V.

	Equiva. NaOH.	0.1.	0.25.	0.5.	0.75.	1.0.	1.25.	1.5.	1.75.
Magnesium.	Hydrogen electrode : 100 c.c. 0.025 <i>M</i> MgSO ₄ with 0.099 <i>N</i> NaOH.								
1a.	p_H $L \times 10^9$	10.57 1.3	10.64 1.6	10.67 1.4	10.69 1.3	10.75 1.2	10.80 1.1	10.86 1.0	11.12 1.5
1b.	Glass electrode : 100 c.c. 0.025 <i>M</i> MgSO ₄ with 0.1 <i>N</i> NaOH.								
	p_H $L \times 10^9$	10.69 2.2	10.70 2.3	10.75 2.2	10.80 2.3	10.86 2.3	10.90 2.3	11.00 2.4	11.13 1.8
Manganese.	Hydrogen electrode : 100 c.c. 0.024 <i>M</i> MnCl ₂ with 0.090 <i>N</i> NaOH.								
2.	p_H $L \times 10^{18}$	8.63 2.3	8.76 3.7	8.90 5.8	8.99 6.9	9.03 6.6	9.05 5.7	9.11 4.8	9.37 9.1
Cobalt.	Hydrogen electrode : 100 c.c. 0.0247 <i>M</i> CoCl ₂ with 0.090 <i>N</i> NaOH.								
3.	p_H $L \times 10^{18}$	6.95 1.0	7.07 1.5	7.29 3.2	7.50 6.5	7.64 8.7	7.80 11.5	8.09 20.9	—
Nickel.	Hydrogen electrode : 100 c.c. 0.025 <i>M</i> NiCl ₂ with 0.0967 <i>N</i> NaOH.								
4.	p_H $L \times 10^{18}$	6.76 0.3	6.92 0.6	7.04 0.9	7.13 1.0	7.30 1.5	7.46 1.8	7.69 1.9	—
Ferrous.	Hydrogen electrode : 100 c.c. 0.025 <i>M</i> FeSO ₄ with 0.099 <i>N</i> NaOH.								
5.	p_H $L \times 10^{17}$	5.93 0.09	6.28 0.4	6.78 3.1	7.18 15	7.47 40	7.72 78	7.95 100	—
Lead.	Quinhydrone electrode : 100 c.c. 0.005 <i>M</i> Pb(NO ₃) ₂ with 0.1 <i>N</i> NaOH.								
6.	p_H $L \times 10^{17}$	6.00 0.03	6.60 0.4	—	6.80 0.5	7.26 2.9	7.75 135	—	—
Copper.	Quinhydrone electrode : 100 c.c. 0.005 <i>M</i> CuSO ₄ with 0.1 <i>N</i> NaOH.								
7.	p_H $L \times 10^{20}$	5.37 1.4	5.40 1.4	—	5.47 1.2	5.56 1.2	5.74 13	—	—
Aluminium.	Glass electrode : 100 c.c. 0.00343 <i>M</i> Al ₂ (SO ₄) ₃ with 0.194 <i>N</i> NaOH.								
8.	p_H $L \times 10^{22}$	—	4.17 0.5	4.23 0.7	4.28 0.8	4.32 1.0	4.37 1.2	4.43 1.5	4.52 2.1
		2.0 equivs. $p_H = 4.61$. $L = 3.0 \times 10^{-22}$.							
		2.25 " $p_H = 4.81$. $L = 8.0 \times 10^{-22}$.							

Equivs. NaOH for complete precipitation :

2. 1.93. 3. 1.75. 4. 1.66. 5. 1.71. 6. 1.5. 7. 1.5. 8. 2.73.

electrodes, however, appear to have been very easily incapacitated. With such electrodes they observed p_H values that were about 1 p_H unit higher than those obtained by Britton. Incidentally Prytz¹⁰ states that electrodes covered with platinum black give p_H values in the case of the alkali precipitation of zinc chloride solutions that are in good agreement with those found by Kolthoff and Kameda. Moreover, these latter workers obtained similar, though not so accurate, results with the quinhydrone electrode. This is surprising, for in the hands of the authors the quinhydrone electrode always led to higher values. On applying the hydrogen electrode to zinc salt titrations we found that

542 USE OF GLASS ELECTRODE IN TITRIMETRIC WORK

during the passage of hydrogen through the titration vessel, E.M.F.'s are established similar to those observed by Britton. If, however, much time is allowed after stopping the flow of hydrogen, there is a gradual drift in potential towards the higher p_H values recorded by Kolthoff and Kameda. Such potentials are extremely unsteady, and the apparent p_H values become smaller immediately the film of liquid in direct contact with the platinum black is disturbed.

A series of zinc salt solutions was titrated in the glass cell at room temperature. Details of these titrations are given in Table VI, and the actual curves are plotted in the lower part of Fig. 3. The two titration curves of the more concentrated zinc salt solutions were confirmed with the quinhydrone electrode. 1.53 equivalents of alkali precipitated all the zinc as basic zinc sulphate from the 0.025*M* solution and 1.82 equivalents from the 0.0025*M* zinc sulphate solution, but almost the whole of the stoichiometrical quantities of sodium hydroxide was required to complete the precipitations from the two zinc chloride solutions.

TABLE VI.—PRECIPITATION BY SODIUM HYDROXIDE FROM ZINC SALT SOLUTIONS.

Equivs. NaOH.	0.1.	0.2.	0.4.	0.6.	0.8.	1.0.	1.2.	1.4.	1.6.	1.8.
1. 100 c.c. 0.025 <i>M</i> ZnSO ₄ with 0.1 <i>N</i> NaOH.										
p_H	6.77	6.83	6.89	6.96	7.04	7.17	7.30	7.71	—	—
$L \times 10^{17}$	3.2	3.8	4.0	4.4	4.8	6.0	6.6	17	—	—
2. 100 c.c. 0.0025 <i>M</i> ZnSO ₄ with 0.01 <i>N</i> NaOH.										
p_H	7.36	7.41	7.56	7.63	7.755	7.88	7.98	8.11	8.31	—
$L \times 10^{17}$	4.8	5.6	9.3	10.5	14.8	20.9	24.0	28.2	36.3	—
3. 100 c.c. 0.01 <i>N</i> HCl, 0.025 <i>M</i> ZnCl ₂ with 0.2 <i>N</i> NaOH.										
p_H	7.13	7.24	7.38	7.42	7.49	7.57	7.62	7.72	7.82	8.15
$L \times 10^{17}$	17.0	25.1	41.7	42.7	49.0	58.9	57.5	67.6	69.2	155
4. 100 c.c. 0.001 <i>N</i> HCl, 0.0025 <i>M</i> ZnCl ₂ with 0.02 <i>N</i> NaOH.										
p_H	7.45	7.60	7.74	7.84	7.92	8.00	8.06	8.13	8.26	8.42
$L \times 10^{17}$	6.9	13.2	21.9	29.5	35.5	42.7	43.7	44.7	52.5	53.7

Fig. 3 and Table VI show that precipitation took place from the 0.025*M* ZnSO₄ at a somewhat lower p_H than from the corresponding solution of zinc chloride. It is also seen that the concentration of the salt solutions has a marked effect on the p_H range within which the major part of the precipitation took place.

Kolthoff and Kameda's method of preparing extremely pure crystalline zinc sulphate by the repeated recrystallisation at 0° of solutions that had been saturated with zinc sulphate at the abnormally high temperature of 70° is open to criticism. At 70° hydrolysis of these solutions must have been appreciable, and this would be accompanied by the passage into colloidal solution of some basic zinc sulphate. On cooling, some of the suspended basic zinc sulphate would contaminate the zinc sulphate crystals, and would thus explain the exceptionally high p_H values which Kolthoff and Kameda observed for their solutions, e.g., 5.89 for 0.02*M* ZnSO₄.

In the present work and in the previous work by Britton the "A.R." quality of zinc sulphate was invariably used, but 0.025*M* solutions, prepared at different times, gave p_H values between p_H 3.8 and p_H 5.2. These wide variations may be attributed to the difficulty of preparing crystals of zinc sulphate that are absolutely free from contaminating acid on the one hand and basic matter on the other. Hence, before any accurate determinations of the hydrolysis of zinc sulphate solutions can be made crystals must be employed that were obtained from solutions saturated at the temperature at which the measurements are to be made.

Solubility Products of Basic Precipitates.

In a previous paper Britton showed that the concentration of metal ions that *actually took part* in the initial separation of a basic precipitate and the concentration of the hydroxyl ions of the solution gave rise to ionic products, $[Mg^{++}][OH']^2$ and $[Mn^{++}][OH']^2$, that were in agreement with the values of the respective solubility products which had been obtained by other workers using conductivity measurements. Such computations, however, do not give values of the true solubility product, for no account is taken of the metal ion concentration of the mother-liquor. If the variation in the p_H throughout the precipitation is determined by the solubility product of the base, then it would be expected that the relationship, $[Me^{++n}][OH']^n$, would yield a constant value at any stage of the precipitation.

In Tables V and VI values of the respective solubility products are recorded corresponding to the concentrations of metal and hydroxyl ions prevailing during the addition of varying equivalent amounts of sodium hydroxide. Besides the p_H values obtained by the glass electrode, Table V also contains the data corresponding to curves already described by Britton⁸ and Britton and Meek.²⁰ In order to compute the metallic ion concentrations of those solutions from which basic precipitates separated, the assumption, not always quite justifiable, was made that the composition of the basic precipitate during the gradual addition of alkali was the same as that existing when complete precipitation had taken place. In titrations 1*a* and 1*b*, Table V, it was assumed that no magnesium sulphate was entrained by the precipitates. The fact that some was carried down is not markedly reflected in the inflexion of the glass electrode curve in Fig. 3. The values of L remained remarkably constant, although the mean value given by the hydrogen electrode curve was 1.3×10^{-9} , whereas that given by the glass electrode titration was slightly higher, *viz.*, 2.2×10^{-9} . With the possible exceptions of nickel, copper, and lead, the solubility products show no constancy but increase with the amount of alkali added. This is very pronounced in the cases of $[Fe^{++}][OH']^2$, the value of which rapidly increased from 9×10^{-19} to 1×10^{-15} , and of $[Pb^{++}][OH']^2$, which ranges from 3×10^{-19} to 1.35×10^{-15} .

Similarly in the zinc salt solutions (Table VI) it is seen that the solubility product principle is not obeyed, at any rate when applied to the zinc and hydroxyl ions. Kolthoff and Kameda calculated the value of $[Zn^{++}][OH']^2$ to be 1×10^{-17} , using the p_H value prevailing at the point of initial precipitation in zinc sulphate solution, whilst

Prytz from the p_H value set up when one equivalent of alkali had been added to a zinc chloride solution gave the value 1.29×10^{-17} .

The value of $[Mg^{++}][OH']^2$ is usually considered to be 3.4×10^{-11} at 18° as indicated by the conductivity measurements of Kohlrausch and Rose.³⁰ The values now obtained are very much larger. A perusal of the solubility figures given for magnesium oxide obtained by direct analysis,³¹ shows a wide variation in the recorded values. The data of Fresenius, however, lead to 1.35×10^{-9} , which is similar to that obtained by the authors.

Applebey and Reid³² give figures for $[Pb^{++}][OH']^2$ based on the potentials of lead electrodes immersed in sodium hydroxide solutions saturated with various forms of lead monoxide. Thus at 20° they obtained 4.7×10^{-16} and 9.1×10^{-16} . Table V, however, shows that very different values hold during the basic precipitation of a lead nitrate solution.

Randall and Frandsen³³ have summarised the various published values of $[Fe^{++}][OH']^2$. They range from 1.6×10^{-19} to 1.6×10^{-14} . Table V shows that the values for the different stages of the precipitation of basic ferrous sulphate ranged from 9×10^{-19} to 1×10^{-15} .

If the solubility products of metallic hydroxides are to have any real significance, it is essential that they should have direct bearing on the ionic concentrations prevailing during their precipitation. With the exception of silver hydroxide, it is by no means certain that any such relationship exists. From the results given in Tables V and VI, it would appear that the solubility product principle cannot be applied to precipitations of basic salts, whether they are of definite or indefinite composition.

Summary.

(1) The most convenient method of calibrating the glass electrode for general use consists of titration of a universal buffer solution.

(2) A critical examination has been made of the use of the electrode in titrimetric work, with the following results:—

(a) Accurate p_H values are registered in buffered solutions, ranging from p_H 2 to p_H 12.

(b) The errors accompanying the titration of unbuffered solutions are confined to the narrow regions in which wide variations of the p_H value occur.

(c) The presence of precipitates does not interfere with the accuracy of the electrode.

(3) p_K values of a number of acids, many of which have not been accurately measured before, have been determined.

(4) Computation of the solubility product of silver hydroxide from the glass electrode p_H values leads to a value in agreement with previous data.

(5) It has not been found possible to reproduce the p_H curves corresponding to the titration of zinc salts with alkali reported by Kolthoff and Kameda, and also by Prytz.

(6) It has been found that although the solubility product principle applies to the precipitation of silver hydroxide, and possibly to the precipitation of magnesium hydroxide, the principle is untenable in the case

³⁰ *Z. physikal. Chem.*, **12**, 241, 1893.

³¹ See Mellor, *Comprehensive Treatise of Theoretical and Inorganic Chemistry*, Vol. IV., p. 289.

³² *J. Chem. Soc.*, **121**, 2129, 1922.

³³ *J. Amer. Chem. Soc.*, **54**, 46, 1932.

of the formation of basic precipitates generally. The use of the p_H value prevailing at a single point in such a precipitation cannot therefore be expected to lead to an accurate knowledge of the true solubility product.

In conclusion the authors wish to express their indebtedness to the Government Grant Committee of the Royal Society and to the Chemical Society for grants which have defrayed part of the cost of the instruments, and also to the Advisory Council of the Department of Scientific and Industrial Research for a grant.

*Washington Singer Laboratories,
University College of the South-West of England,
Exeter.*

THE ABSOLUTE MEASUREMENT OF THE AVAILABLE ENERGY OF HIGH EXPLOSIVES BY THE BALLISTIC MORTAR.

BY W. TAYLOR AND G. MORRIS.

Received 10th March, 1932.

The maximum mechanical work available from highly compressed hot gas mixtures has formed the subject of numerous investigations in connection with internal combustion engines and also with the internal ballistics of guns. These studies acquire additional interest owing to their intimate relationship with the question of the specific heats of gases at temperatures and pressures which are too high to be easily treated by direct experiment.

The maximum work capable of being performed by high explosives is governed by the same underlying principles, but by contrast with what has been accomplished in the other two fields, precise methods of measurement have not been developed to anything like the same extent. The present paper deals with a preliminary effort to establish the subject upon a more scientific basis.

Manufacturers and users of high explosives in the past have relied largely upon the popular Trauzl Lead Block test, and to a lesser degree upon the official pendulum test. Neither of these lends itself to interpretation in terms of absolute units and known conditions of experiment.

In recent years, however, the ballistic mortar test has enjoyed an increasing popularity in Great Britain and U.S.A. in preference to the lead block test as a means for comparing the strengths of blasting explosives. The advantages claimed for the mortar are that it furnishes more regular results, is less affected by irrelevant variables, and that the results admit of a more precise specification in absolute units.

A study has recently been made at the Research Laboratories at Ardeer with the object of developing the theory of the mortar test, and also of ascertaining how nearly the working of the actual test approaches ideal conditions.

The essential principle of the mortar test is that the explosive, instead of being caused to do work against a varying and unknown resistance as in the lead block, is fired in a suitable type of gun so that

the work done in the expansion of the products of detonation may be measured in absolute mechanical units. The interpretation of the test involves, therefore, the consideration of the principles of ballistics as applied to the special conditions ruling in the mortar. It will be noted that the estimation of the strength of the explosive from its ballistics is the reverse problem to that usually required in artillery work. There is in addition the further problem of deciding how far the energy constants of the explosive so determined are related to the useful work which is likely to be obtained from the explosive in practice.

Dealing first with the test itself, the treatment falls naturally under three headings, firstly, the mechanics of the apparatus itself, and the method of estimating the total mechanical energy yielded by the explosive, secondly, the ballistic theory for an ideal mortar, and finally, the effects of the factors which reduce the theoretical efficiency, for example, the energy losses due to cooling by the walls, gas leak, and frictional resistance.

1. Mechanical Details of the Apparatus.

The original form of the ballistic mortar was described by Comey.¹ A replica of this mortar was installed at Ardeer several years ago, and was extensively used in the present research. In addition, a more precise instrument has been erected recently: this will be referred to as the "new" mortar.

In both cases, the essential features are a massive mortar slung as a ballistic compound pendulum, and a recording device which automatically registers the angle of recoil. The latter may easily be read to two minutes of arc.

The explosive under test is made to fire a projectile weighing $36\frac{1}{2}$ lbs. into a sand heap, and measurements are made on the recoiling mortar, this being more convenient in practice than observations of the flight of the projectile. The usual charge of explosive is 10 grams, initiated by a commercial No. 6 detonator containing 1 gram of a mixture of mercury fulminate and potassium chlorate.

The dimensions and masses of the two instruments are summarised in the following table, and the arrangement of projectile and firing chamber is shown in Fig. 1.

TABLE I.

Dimension.	Old Mortar.	New Mortar.
Weight of mortar	473 lbs.	733 lbs.
Weight of suspension	349 "	295 "
Weight of projectile	36.5 "	36.5 "
Depth (S) of centroid below axis of suspension	7.91 feet	8.84 feet
Length (L) of simple equivalent pendulum	9.51 "	9.85 "
Depth (r) of axis of firing chamber below axis of suspension	10 "	10 "

For a compound pendulum of this type, one of the most important requirements is that the centre of percussion should coincide with the axis of the firing chamber, otherwise an impulsive shock is delivered at

¹ *Proc. 8th Congress Applied Chemistry*, 25, 209, 1912.

the axis of suspension, and a portion of the energy which should contribute to a smooth swing of the pendulum is wastefully dissipated. In the old mortar, this condition is not strictly fulfilled, the centre of percussion being about 6 ins. from its correct position, and this defect is manifested on firing by severe vibrations in the suspension bars. A calculation of the effects of the misplaced impact showed that about 5 per cent. of the energy communicated to the pendulum could be dissipated in this way. The new mortar is sensibly free from the defect.

The mechanical theory of the pendulum is simple. Consider the system at the instant the projectile has left the barrel of the mortar,

and let Q be the total energy received by the mortar and projectile together at this instant. The bulk of the energy is vested in the projectile on account of its smaller mass, m . If v is the velocity of ejection, the kinetic energy of the projectile is $\frac{1}{2}mv^2$.

The energy vested in the pendulum is $E = \frac{1}{2}\mathcal{I}\omega^2$, where \mathcal{I} is the moment of inertia about the axis of suspension, and ω is the angular velocity of recoil. The third law of motion demands that the angular momenta of projectile and pendulum should be equal, giving $\mathcal{I}\omega = mrv$, where r has the significance given in Table I. Hence the total kinetic energy of the system at the instant considered is

$$Q = E(1 + \mathcal{I}/mr^2) \quad (1)$$

and for a compound pendulum, $\mathcal{I} = WSL$, the last three quantities being easily determined constants of the pendulum, W being the total mass of the pendulum system.

The value of E in any particular throw may be determined from the throw angle A , since all the energy is expended in doing work against gravity, always assuming that the pendulum functions ballistically. (The latter assumption is valid since the time taken to eject the projectile is about 4 milliseconds whereas the time period of the pendulum is over 3 seconds.) Hence, by a well-known theorem, $E = WS(1 - \cos A)$ and hence the total energy of the system from equation (1) becomes

$$Q = Q_0(1 - \cos A) \quad (2)$$

$$Q_0 = WS(1 + \mathcal{I}/mr^2)$$

For the old mortar, $Q_0 = 52.04$ ft.-tons, or 116,500 ft.-lbs., while for the new mortar, $Q_0 = 103.6$ ft.-tons or 232,000 ft.-lbs. This equation allows the throw angle A to be converted immediately into absolute units of kinetic energy. It is assumed that no energy is imparted to the pendulum after the projectile has cleared the barrel and the gases expand freely into the atmosphere. Experiment shows that this assumption involves no perceptible error; the reaction of the air alone to the efflux of gas is unable to swing the pendulum to any appreciable extent, so that the equation of momentum needs no correction.

It will be observed that on account of the different values of Q_0 for

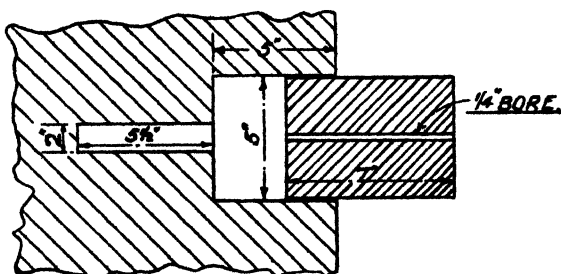


FIG. 1.—Showing inner dimensions of mortar with projectile partially ejected.

the two pendulum systems, the throws will be different even when explosives are made to deliver identical quantities of energy Q , to each. As will be shown, in the discussion of ballistic theory, this should be the case when equal charges of the same explosive are fired in the two mortars. The following experimental results show how far the Q values and the throws do compare in practice. The explosive was 10 grams of T.N.T. initiated by the standard detonator used in the working of the test.

TABLE II.—COMPARISON OF RESULTS ON THE TWO MORTARS.

	Old Mortar.	New Mortar.
Actual throw angle A .	20° 42'	15° 13'
Value of $(1 - \cos . A)$.	0.0624	0.0331
Total energy Q in foot-lbs. .	7270	7680

The results obtained on the new mortar were found to be on the average about 6 per cent. higher than those obtained with the old mortar. It has already been remarked, however, that the result of the misplaced impact in the case of the old mortar should lower all results by about 5 per cent., and hence the above agreement was regarded as quite satisfactory and within the limits of experimental variation.

Incidentally, it may be remarked that a variation in the mass of the projectile exerts a large influence on the throw, as will be apparent later when discussing some results obtained with a duralumin projectile. With a projectile weighing 9.8 lbs., the recoil was reduced from 17° 45' to 9° 43' but the Q values remained the same within the limits of experimental variation.

2. Ballistic Theory.

The object of ballistic theory is to relate the total energy Q which is experimentally obtained in the manner just described with the properties of the explosive, and the conditions under which the latter is fired.

At the very outset, a great simplification is introduced by the consideration that the explosive is wholly consumed before the projectile has moved appreciably. Assuming a maximum length of 3 cm. for the 10-gram charge, and a velocity of detonation in the neighbourhood of 3000 m. per second, the detonation will only take about 0.01 milli-second for completion, and even if the projectile commenced to move with its final velocity of 100 feet per second, it would only have travelled about 0.01 inch in that time. Thus, the rate of burning, a factor which introduces many complications into ordinary ballistic theory, can be entirely eliminated here, and the problem takes the simple form treated in the classical paper of Nobel and Abel² in which they assumed that the rate of burning of certain types of gunpowder was infinitely great.

The work done by the explosive is due to the adiabatic expansion of the hot gaseous products of the detonation; the effect of any non-gaseous products being to increase the heat content of the gases. In virtue of the high rate of detonation, these gases may be assumed to

² *Phil. Trans. Roy. Soc.*, 1875.

commence their operations at what is virtually the pressure they would exert in a closed vessel of the same dimensions as the firing chamber of the mortar, say V_0 . The gases continue to expand and to do work upon the projectile until the latter leaves the mortar, at which instant they occupy a final volume V , and are then liberated without doing further work on the system. In other words, the mortar behaves like an internal combustion engine working through a single expansion between the volumes V_0 and V .

The internal dimensions of both mortars are practically the same, the firing chambers being cylindrical, $5\frac{1}{2}$ ins. long, and 2 ins. in diameter, while the outer barrels are 5 ins. long and 5 ins. in diameter. The values of V_0 and V are therefore 16.5 and 114.7 cubic ins. respectively, and the expansion ratio, $R = V/V_0 = 6.95$, or approximately 7. Since the charge is only 10 grams, it will be noted that the loading density is quite small, namely, 0.037 grams/c.c.

The work done in an adiabatic expansion is given by

$$Q = p_0 V_0 (1 - 1/R^n)/n \quad (3)$$

which may be referred to as the internal ballistic equation. Here R is the expansion ratio, and n is equal to $m - 1$, where m is the ratio of the specific heats at constant pressure and constant volume, averaged over all the components of the mixture. The value of m depends upon the nature of the products themselves; for ideal monatomic gases, $m = 1.67$ while for the products from gunpowder, Nobel and Abel found $m = 1.32$, and Hopkinson³ gives $m = 1.24$ for the explosion products in an internal combustion engine which presents a strictly analogous problem.

The factors which govern the work done by the explosive are therefore the expansion ratio R , the exponent n , and the product $p_0 V_0$, which for unit charge is often referred to as the "force" or "characteristic product" of the explosive. Of these three factors, R is determined solely by the geometry of the mortar, and n is characteristic of the explosive only. The product $p_0 V_0$ is also characteristic of the explosive, and is sensibly independent of the initial volume V_0 so long as the loading density is not too high and V_0 is not varied so widely as to cause a different equilibrium of the products. The expansion of the gases from the original volume occupied by the explosive to the volume V_0 is sensibly isothermal as the work done in compressing the air is negligible.

It follows that if R is altered, as for example, by changing the internal dimensions of the mortar, the total energy Q delivered to the system will also be altered in a manner indicated by the last equation above. Mortars of the same internal dimensions will, however, receive equal quantities of energy from equal charges of explosives, although the actual partition between pendulum and projectile may differ according to their relative masses. In particular, since the two mortars at Ardeer have the same initial and final volumes, the Q values obtained on each should agree, and, as has been shown above, this is actually the case.

3. Experimental Verification of the Internal Ballistic Equation.

It seemed desirable in the first instance to determine whether the projectile, in passing along the barrel of the mortar did in fact receive

³ *Proc. Inst. C.E.*, 169, 160, 1907.

energy from the explosion products at the rate given by the internal ballistic equation. It might well happen for example that the chemical or physical changes taking place during the expansion might introduce variations in practice.

For this purpose it was desired to know the velocity of the projectile at various distances along the barrel. As the total distance traversed in the mortar was only 5 ins., methods of obtaining the displacement-time curve were rejected in favour of a simple direct procedure, the principle of which was that if a large number of mortars could be provided, each with a different length of barrel, then the emergence velocities of the projectiles in each case could readily be deduced from the corresponding pendulum swings. The assumption was then made that the emergence velocity for a barrel of 2 ins. would be exactly the same as

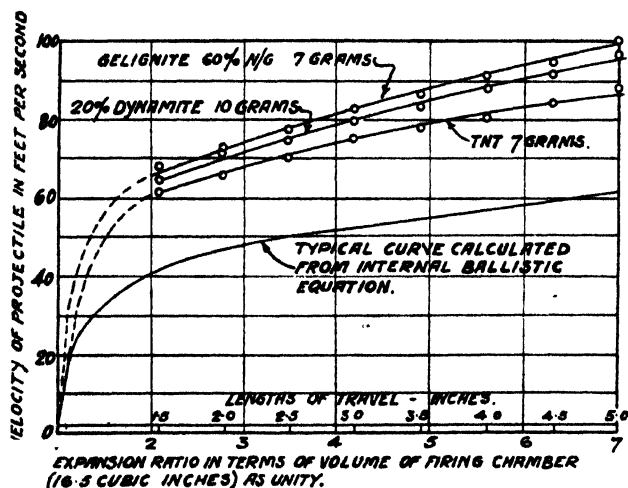


FIG. 2.—Velocity of projectile as a function of its travel along the barrel of the mortar.

The velocity acquired by the projectile is shown for various expansions of the gases inside the mortar; a scale has also been given to show the corresponding lengths of travel which the projectile has moved through.

The lowest curve has been calculated from the theoretical equation to show that it is of the same form: the ordinates can be multiplied at will by assuming different values of charge. Note the large increase of velocity in the first inch of travel.

firing chamber unaltered.

The results of these experiments are given in the following table, and shown graphically in Fig. 2.

The variation of Q with the expansion ratio R can be expressed very conveniently over the experimental range by the empirical relation

$$Q = Q_1 \left\{ \frac{(R-1)}{(R_0-1)} \right\}^p \quad \text{where } R_0 \text{ is the normal ratio } 7, Q_1 \text{ is the energy}$$

obtained on the normal mortar, and p is a constant, characteristic of the explosive. This form was found to give a more amenable equation for fitting constants, and a curve obtained from it was very near to the corresponding one obtained from the internal ballistic equation. For example, the results of a particular set of experiments were found to be expressed by $Q = 5.34 (1 - R^{-0.6})$ and also to the same degree of ap-

the velocity acquired by the projectile after travelling 2 ins. along the standard 5-in. barrel, and in this way the velocities corresponding to a number of travel-lengths could be determined.

The provision of a number of mortars of different barrel lengths was realised experimentally by fitting a number of plugs and liners inside the old mortar; these effectively reduced its length, while leaving the volume of the

TABLE III.—VELOCITIES OF THE PROJECTILE AT VARIOUS STAGES OF ITS TRAVEL BEFORE LEAVING THE BARREL.

7-gram charges were used for the gellignite and TNT, and 10-gram charges for the 20 per cent. dynamite. The experiments were carried out in the old mortar, the energies Q being deduced from the throw angle in the usual way, and the emergence velocities from the formula $v = \sqrt{\frac{2WSJg(1 - \cos A)}{m^2v^2}}$.

Length of Travel, (ins.).	Expansion Ratio, $R = V/V_0$.	Gellignite, 60 Per Cent. Nitroglycerine.		Woodmeal Dynamite, 20 Per Cent. Nitroglycerine.		T.N.T.	
		Energy, Q ft./lbs.	Velocity of Projectile, v ft. per sec.	Q .	v .	Q .	v .
5.0	6.95	6020	100.2	5600	96.3	4680	87.9
4.5	6.26	5480	95.3	5010	91.4	4210	83.6
4.0	5.56	5070	91.8	4750	88.8	3920	80.8
3.5	4.87	4480	86.1	4180	83.1	3630	77.8
3.0	4.17	4150	82.9	3850	79.9	3400	75.0
2.5	3.47	3660	77.9	3460	75.7	2970	70.1
2.0	2.78	3200	72.8	3100	71.6	2660	66.4
1.5	2.08	2800	68.3	2530	64.9	2300	61.8

proximation by the internal ballistic equation $Q = 2.47 (R - 1)^{0.182}$.

The values of p for various explosives were as follows: Tetryl 0.378, picric acid 0.620, T.N.T. 0.630, blasting gelatine 0.513. It appeared to be higher for those explosives having solid residues than for fully balanced explosives with gaseous explosion products only, but too much stress cannot be laid on this point.

The experiments were carried out with a number of different explosives, but in all cases the results were of a similar nature. It was concluded, therefore, that the behaviour of the explosion gases in the mortar, and the

mechanical work done on the mortar system was in reasonably good

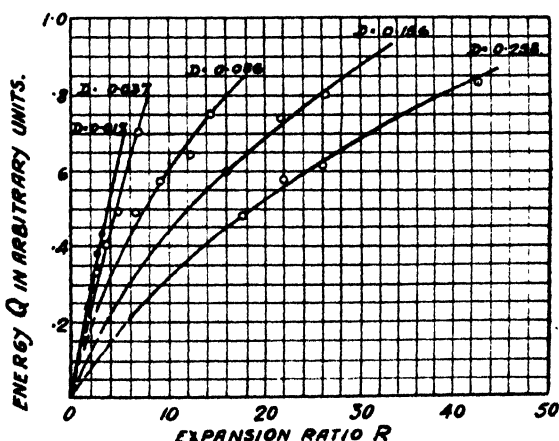


FIG. 3.—Showing variation in energy yielded by the explosive at different loading densities in the mortar.

The energies are expressed in arbitrary units, viz.: $(1 - \cos A)$ where A is the angle of throw of the pendulum. They may be converted into absolute values by multiplying by the appropriate value of Q_0 for the old mortar, i.e. 52.04 foot/tons.

Note that at low loading densities in the region of $D = 0.037$ the normal value for the mortar, the effect of changes in loading density is small. To obtain the formal relation between D and Q for constant R , the reciprocals of the energies, viz., $1/Q$ were plotted against D and yielded a set of straight lines converging at a point on the D axis on the negative side. The general formula was therefore $Q(D + d) = \text{constant}$ where d was the common intercept.

552 ENERGY OF HIGH EXPLOSIVES BY BALLISTIC MORTAR

agreement with the theoretical equation so far as the normal mortar was concerned.

When, however, the results obtained with different initial loading densities were compared, appreciable discrepancies were observed; for example, if the expansion ratio R were kept constant, but the volume of the firing chamber, V_0 , were changed by means of a plug, the total energy Q was no longer the same, and the theory apparently broke down. To illustrate the actual behaviour, the following table shows results obtained with Rockite, an ammonium nitrate explosive, the general characteristics being shown conveniently in Fig. 3.

TABLE IV.—EFFECT OF INITIAL LOADING DENSITY.

Old mortar. Explosive = Rockite, containing 10 per cent. nitroglycerine, 80 per cent. ammonium nitrate and 10 per cent. woodmeal. 10-gram charges primed with standard No. 6 detonator.

Initial Volume of Firing Chamber, V_0 in c.c.	Loading Density, D , grams/c.c.	Expansion Ratio, R .	Value of $(1 - \cos A)$ where A = Angle of Recoil.
270	0.037	7.0	0.0701
		4.6	0.494
		3.4	0.402
		2.8	0.338
38.4	.258	42.7	0.831
		26.1	0.613
		21.9	0.566
		17.7	0.475
64	.156	26.4	0.805
		21.1	0.738
		16.1	0.609
115	.0865	14.9	0.759
		12.2	0.643
		9.4	0.580
		6.6	0.487
588	.017	3.25	0.430
		2.64	0.373
		2.09	0.288
		1.82	0.237

Similar results were obtained with a variety of explosives, and the conclusion can be expressed briefly by saying that in practice, the energy Q received by the mortar system is not independent of the initial volume of the firing chamber as would be expected from theory; instead, there is a relation between the loading density D , and the energy Q , which, on analysis was found to be of the type ⁴

$$Q = \text{Constant} \div (D + d)$$

⁴ This equation may obviously be written as $Q = Q_1 \frac{(D_0 + d)}{D + d}$ where Q_1 is the energy obtained from the given explosive on the normal mortar for which $D_0 = 0.037$ grams/c.c. The energy Q is then obtained when the expansion ratio remains unchanged namely 7, but the loading density has been altered to D grams/c.c. The values of the small constant d were as follows: blasting gelatine 0.069, picric acid 0.041, T.N.T. 0.045.

where d is a small constant varying slightly from one explosive to another. The correction is, however, small for the normal loading density, namely, 0.037 gram/c.c. By applying the above equation, all the family of curves shown in Fig. 4 could be reduced to a single curve giving the relation between R and Q for a standard loading density.

4. Variation of the Total Energy Q with Charge of Explosive.

The product $p_0 V_0$ in the internal ballistic equation is proportional to the charge of explosive for loading densities of the magnitudes considered here. The Q values obtained from the mortar should, therefore, be proportional to the charge, but subject to a constant increment contributed by the detonator itself. On plotting the energy against the charge, a straight line should be obtained cutting the Q axis at an intercept value equal to the detonator contribution.

A series of experiments with different explosives showed that this was not the case in practice. The graphs were not perfectly straight

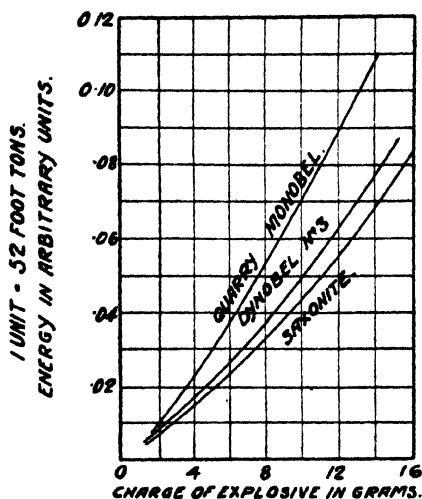


FIG. 4 (a).—Variation of energy with charge of explosive fired in mortar.

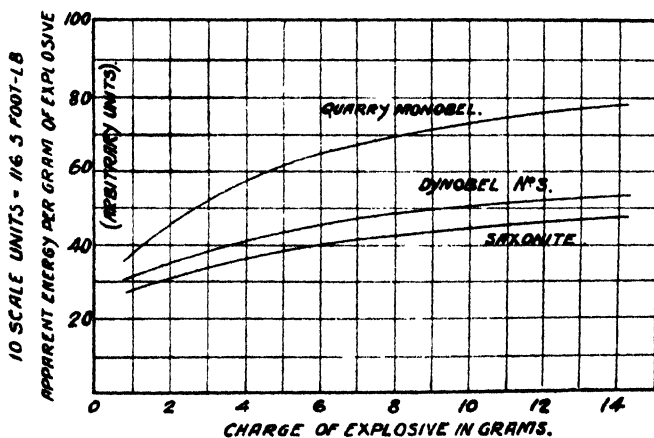


FIG. 4 (b).—Derived curves showing rise in the apparent energy per gram of explosive as the charge is increased. These values are derived from those of Fig. 4 (a).

lines, and on being produced backwards to cut the Q axis, made very small, and sometimes even negative intercepts. The curvatures of these graphs was most marked in the region near the origin, and were slightly different according to the explosive under test. As examples of the results obtained, a number of typical curves are shown in Figs. 4 (a) and 4 (b), and a complete set of experimental values is reproduced in Table V below.

The curvature is in a different direction to that which would be expected from the loading density effect discussed above, but the contribution of the latter is small for charges up to 10 grams in the normal mortar, and does not enter appreciably into these results.

It follows that the apparent energy per gram of explosive varies according to the charge selected for the test; to illustrate this, the apparent energy per gram has also been plotted against the charge in Fig. 4 (*b*).

5. Departure of the Actual Mortar from Ideal Conditions.

From the experimental work just described, it would appear that, while there is a general agreement between the results obtained in practice and the simple ballistic theory, there are some outstanding discrepancies, namely:—

(1) The energy delivered by the explosive is not independent of the loading density D , but falls off quite seriously for large values of D .

(2) The energy is not simply proportional to the weight of charge used, but falls off appreciably at low charges; a quantity of energy always seems to be lost, the fraction of the total energy so lost being high for charges of 1, 2 or 3 grams, and approximating to about 10 per cent. for the 10-gram standard charge, notwithstanding that the detonator itself contributes energy to the mortar.

The explanation of these effects is to be found in the perturbing influences experienced in all guns, some of which are intensified under the peculiar conditions of the mortar test. The chief of these influences are:—

(a) The chilling of the hot explosion gases by the metal walls of the firing chamber and mortar barrel.

(b) Gas leak between the sides of the projectile and the barrel.

(c) Frictional resistance to the motion of the projectile.

(d) Contributions due to the primer.

These may conveniently be considered in the above order.

(a) Heat Loss due to Cooling by the Walls.—The wall area of the firing chamber is 40 sq. ins. initially, and 150 sq. ins. just before the gases are released, while the gases range in temperature from 1500° C. to above 4000° C., so that even in a time of only 4 milliseconds it is evident that an appreciable heat exchange may occur. Furthermore, the wall of the firing chamber becomes greatly pitted and roughened with use, so that the actual cooling surface is much greater than the superficial area.

The loss of energy indicated by the experiments with various weights of charge must undoubtedly be ascribed to heat loss. A rough physical treatment led to a formal equation which was found to be an excellent empirical fit to all the experimental results, and this equation may be adopted as a convenient algebraic expression describing the relation between weight of charge and energy yielded to the mortar system. It is

$$Q = kw - C(1 - e^{-aw}) \quad . \quad . \quad . \quad (4)$$

where w is the weight of charge, k is the "true" energy per gram of explosive free from cooling correction, and C and a are constants depending upon the explosive, e being the base of Napierian logarithms. For values of w above 4 grams, the constants are such that the term in the bracket becomes sensibly equal to unity, and the graph is a straight

line represented by $Q = kw - C$. The magnitude of C is obviously k times the weight of that part of the explosive which appears to contribute no energy to the mortar. As an example of the agreement of this formula with the observed results, Table V shows a series of values obtained with gelignite.

TABLE V.—VARIATION OF ENERGY RECORDED BY MORTAR WITH WEIGHT OF CHARGE OF EXPLOSIVE.

Also showing comparison between observed results and those calculated from the empirical formula (4) of text.

Weight of Charge (grams) (Gelignite).	Observed Energies Expressed as $(1 - \cos . A)$.	Energies Calculated from Formula.	Difference.
0.2	0.0009	0.0009	0.0000
0.4	.0015	.0019	.0004
0.6	.0028	.0028	.0000
0.8	.0037	.0038	.0001
1.0	.0045	.0049	.0004
1.3	.0063	.0067	.0004
1.7	.0088	.0089	.0001
2.0	.0107	.0108	.0001
2.5	.0137	.0142	.0005
3.0	.0179	.0174	— .0005
4.0	.0245	.0246	.0001
5.0	.0305	.0321	.0017
6.0	.0411	.0398	— .0013
7.0	.0467	.0462	— .0005
8.0	.0526	.0547	.0021
9.0	.0642	.0632	— .0010
10.0	.0715	.0717	.0002
11.0	.0817	.0802	— .0015
12.0	.0871	.0889	.0016
13.0	.0984	.0972	— .0012
14.0	.1043	.1057	.0014
15.0	.1163	.1143	— .0020

The values of the constants used in the empirical equation were $k = 0.00851$, $C = 0.0134$, $a = 0.305$. The "true" value for the energy per gram of the gelignite was therefore $0.00851 \times 116,500 = 991$ foot-lbs. per gram.

(b) **Gas Leak.**—The possibility of gas leakage from the mortar is greatly enhanced by the fact that the projectile is drilled axially to take the time fuse used for firing the charge. Furthermore, the clearance between the projectile and mortar extends round a circumference of nearly 20 ins. On the other hand, the driving pressure is small relative to that obtaining in artillery so that the factors affecting gas leak do tend to balance one another to some extent under normal firing conditions.

The fuse hole is $\frac{1}{4}$ -in in diameter, but at the moment of firing, it is filled with a hot plastic mass, the residue of the burnt fuse. When firing low charges, it is sometimes found that this is not ejected, but has formed a tightly pressed plug requiring to be drilled out. It is evident then that in the first stages of the action at least, the central hole is closed by an effective gas check.

With higher loading densities, and therefore higher gas pressures, the fuse acts as a safety valve which blows out and to some extent relieves the pressure inside. The quantity of gas which escapes will be proportional to some power of the loading density. If the projectile

were to move more rapidly, the time for the gas escape would be lessened, and the energies yielded to the mortar would be correspondingly greater. The time of ejection of the projectile depends upon its mass, and it is easy to imagine that in the limit, if the projectile were made sufficiently massive, it would not be ejected at all, but the whole of the gas would stream out through the fuse hole.

It was suggested, therefore, that if the above views were correct, then the losses of energy at high loading densities would be reduced by using a much lighter projectile. The experiment was tried by way of verifying the theory, and a special projectile was constructed of duralumin, drilled internally so as to be partly hollow, and to combine the minimum weight with sufficient strength to withstand the shock of the explosive. This cylindro-conical projectile weighed 9.8 lbs. as against the 36.5 lbs. of the normal one, and the recoil of the mortar was therefore greatly diminished in accordance with the mechanical equation (1) previously derived. In fact, the first shots with the new projectile served as an excellent check upon the mechanical theory, since in spite of the reduced throw angle, the total energy Q should remain the same for a given charge of explosive. The actual agreement was found to be quite satisfactory showing that no appreciable factor has been omitted from the mechanical treatment.⁶

The loading densities were then increased by means of plugs and liners in the same way as previously described, and the ratios of the Q values of the light and heavy projectiles compared. It was found that the ratio became greater as the loading density was increased, until at $D = 0.258$ grams/c.c., it was 21 per cent. greater than at $D = 0.037$ grams/c.c. This was regarded as confirmation of the gas leak hypothesis.

(c) Frictional Resistance to the Motion of the Projectile.—This is very much less in the mortar than in guns where the driving bands on the projectile introduce large resistance factors. The mortar corresponds in fact to an old "smooth-bore" cannon with the further advantage that the whole length of travel is only 5 ins. For these reasons the frictional forces may be regarded as negligible, as they absorb only a few foot-pounds of energy as compared with the thousands of foot-pounds available.

(d) Contribution of the Primer.—The energy contributed by a No. 6 commercial detonator may be estimated by adding extra detonators to a charge of explosive and noting the additional energy yielded to the mortar system. For example, on the old mortar, the mean increment to the value of $(1 - \cos A)$ for a single extra detonator was 0.0025, corresponding to an energy of 290 ft.-lbs. The corresponding angular increment to the throw is of course different according to the magnitude of the throw, but the above increment to $(1 - \cos A)$ was found to be the same whether the extra detonator was added to a small charge

⁶ The details of the comparison were as follows: on the old mortar, the Q_0 value for a projectile of 9.8 lbs. and calculated from equation (1) was 415,500 ft.-lbs.; the average value of $(1 - \cos A)$ per gram given by a certain Glasgow dynamite was 0.00148 giving a total energy $Q = 601$ ft.-lbs. per gram for a normal expansion ratio of 7 and a loading density 0.037 gram/c.c. The mean value of $(1 - \cos A)$ per gram of the same explosive with the normal 36.5 lb. projectile was 0.00504 giving $Q = 588$ ft.-lbs. The agreement was sufficiently satisfactory for work on the old mortar, and for such a wide variation in the mass of the projectile, the difference in the two Q values being only 2 per cent. for a 73 per cent. reduction in m , the mass of the projectile.

giving a throw of a few degrees, or to a strong charge giving 18 degrees or more.

As has been explained before, the effect of the detonator used as primer should be to displace the charge-energy curve parallel to itself so as to give an intercept on the energy axis corresponding to the 290 ft.-lbs. of the detonator. In practice, however, the energy contribution of the detonator is obscured by the effects of the various energy losses.

In addition to the effects of the primer, variations were found to be introduced by the residues left in the firing chamber as a result of previous shots. It was only by scrupulous cleaning of the mortar that this trouble would be minimised, and a useful means to this end was the firing of 5 grams of picric acid alternately with the test shots. Any surplus of the oil used to lubricate the projectile was also found to affect the throw. Finally, the material of the wrapper of the charge of explosive contributes a specific effect.

Slow Time Variations.

Having regard to the above factors, it is not surprising that the mortar should show a slow time variation such as is found in guns. Owing to changes in the projectile clearance, surface wear, etc., the mortar results as expressed in absolute units exhibit a slow progressive decrease with time. It is usual in gunnery to estimate from time to time a "factor of effect" of the gun, and to correct the ballistics accordingly; the same principle can be adopted with the mortar by firing some standard explosive as a control. It was found that on correcting the actual results by reference to a standard explosive, the general time-drift of the mortar values was eliminated, and the explosives under test gave the same mean ratio to the standard whether fired on the old mortar with a loosely fitting projectile or on the new mortar with a projectile having a very small clearance. There only remained then a general scatter of the results about a mean value, the scatter being due to genuine experimental variation. The magnitude of the scatter gives a numerical estimate of the accuracy and repeatability of the test, and may serve to compare it with other tests which essay to measure the same property of the explosive.

An account of the working of the test under the various conditions imposed by these considerations does not fall within the scope of the present paper, but it is very relevant to state the range of experimental variation actually found on analysing the testing station results over a period of more than twelve months working. The figures obtained with samples of ordinary manufactured blasting gelatine may be quoted as an example, the standard explosive used in this case being pure tetryl. The results after correction for the factor of effect showed a percentage standard deviation of 1.30 per cent., which must be regarded as a remarkably low figure for a test of this description.

Comparative figures for other tests are unfortunately not available from the literature, and in this respect, it is to be regretted that writers claiming improvements in testing methods have not given definite statistical figures in illustration of their subject. A deviation of 1.3 per cent. would appear, however, to be considerably less than can be obtained by the most careful work with the Trauzl Lead Block. It is evident that the figure is sufficiently low to permit regularity in explosive manufacture to be assessed.

Summary.

In conclusion, the results of the work may be summarised as follows :

The ballistic mortar permits the "strength" of an explosive to be expressed in absolute units. By the "strength" of an explosive is to be understood the maximum mechanical work which the explosion products are capable of performing when utilised most efficiently in a given expansion. The particular expansion ratio selected is 6.95, and it is unlikely that a greater ratio could be obtained efficiently in practice.

The theory of the mortar is simply that of an internal combustion engine, or of a gun with the provision that the whole of the explosive is converted into its decomposition products before any appreciable mechanical work has been performed.

The full theoretical yield of energy is not actually obtained in the mortar owing to various secondary effects which are described in the paper, *viz.*, heat loss to the walls, gas leakage in advance of the projectile, and effects due to the primer, etc. As a rough approximation, it may be said that about 10 per cent. of the full total is lost when operating the mortar under standard conditions.

If the charge is made too small, or the loading density too great, the losses become much more serious, and quantitative expressions for their variation have been given in the paper.

The mechanical theory has been given together with the appropriate data for the two mortars described in the paper ; it is possible to calculate the conversion factors relating the throws given by mortars of different mass and mechanical construction, and with different projectiles, always providing that the expansion ratio and the initial loading density are kept constant. It has been shown that these conversion factors agree quite well with experiment.

The mortar in its most modern form is an instrument of considerable precision, as is shown by the very low value obtained for the standard deviation of results obtained over a long period, but it must be operated with care, and with a full knowledge of the variations to which it is subject, otherwise it may yield misleading results. As an example, the simple comparison of the quantities of two different explosives giving equal mortar throws may be seen to be slightly fallacious owing to the operation of different cooling effects as illustrated in Fig. 4.

In spite of these imperfections, it appears that the ballistic mortar represents the most accurate and scientific means at the present day of comparing the absolute strengths of blasting explosives, and may be regarded as an essential apparatus for the precise quantitative study of the dynamical properties of such explosives.

The above work was carried out in the Research Department, Nobel Section, Imperial Chemical Industries Ltd., at Stevenston. We are indebted to Messrs. Imperial Chemical Industries Ltd., and in particular to Mr. T. Donaldson and Dr. J. Weir for permission to publish this paper.

REVIEWS OF BOOKS.

Metallurgy of White Metal Scrap and Residues. By E. R. THEWS. (London, Chapman & Hall, Ltd. 1930. Pp. xi + 383. 25s. net.)

In all metal industries, the question of the profitable utilisation of scrap metal is of considerable importance ; when the metal itself is initially rather expensive, the means adopted for dealing with scrap produced during some fabrication process may make all the difference between success and failure—economically—in that process. White metals may be numbered among those whose intrinsic value is

sufficiently great to make the recovery of scrap, and other residues containing them, important financially. Those who seek information as to the most effective means of dealing with such residues will find it in Mr. Thews' book.

White metal alloys may consist of the binary and ternary alloys of tin, lead and antimony, either more or less pure or contaminated with such other metals as copper, zinc, bismuth and arsenic. Their composition may vary considerably and hence the treatment of wastes containing them, in order to produce either relatively pure metals or else alloys having a good economic value, is not always simple. Mr. Thews commences by describing briefly the many classes of such alloys in general use and then proceeds to discuss the methods of dealing with the scrap and the various kinds of furnaces and other equipment suitable for the job.

The book contains much useful information and can be recommended to those (*e.g.*, in large engineering works) who are interested in the recovery of scrap metals.

J. H. G. M.

Impurities in Metals. Their Influence on Structure and Properties. By COLIN J. SMITHELLS, M.C., D.Sc. (Second edition, 1930. London, Chapman & Hall, Ltd. Pp. viii + 190. 18s. net.)

The demand for a second edition of Dr. Smithells' book in a little over two years indicates that there was need for such a book. Actually, of course, the importance of impurities—even when present in minute amounts—on the properties of metals becomes yearly more apparent. In following up the effects of some particular impurity on some specific metal, the investigator may, however, in the eagerness of his work, fail to realise that there is much in common in the action of definite types of impurities on various metals and hence neglect—perhaps remain in ignorance of—investigations on other metals. It is probable that in thus summarising, and whenever possible generalising on, the results obtained on many different metals, will be found the chief value of Dr. Smithells' work. His book makes it evident that in a study of impurities, all metals are concerned; and that the effect produced even by minute amounts are often of the greatest moment in the practical use of metals.

In preparing the new edition, a considerable amount of new matter has been added, particularly as regards the structural effects produced by various gases and the action of impurities in general on mechanical properties. The general plan of the book remains as before; also, as before, there are unfortunately a number of statements regarding matters of detail which, to say the least, are misleading.

J. H. G. M.

Automobile Steels. By Dr. A. MUELLER-HAUFF and Dr. KARL STEIN. Trans. from the German by Dr. H. GOLDSCHMIDT. (New York: J. Wiley & Sons, Inc.; London: Chapman & Hall, Ltd. 1930. 17s. 6d. net.)

The motor industry is second only to the aeronautical in demanding strength combined with lightness in the materials used in fabricating its products. It uses a considerable amount of alloy steels and of specialised types of carbon steels, and economic considerations suggest that the properties and relative merits of these various steels should be thoroughly understood by their users.

Presumably the authors of this book set out to give the industry this information but their efforts, unfortunately, have not been very successful. The book is badly written (and, incidentally, poorly translated) and contains so many inaccurate or misleading statements that a study of its contents is more likely to increase confusion in the reader's mind than to clarify his ideas as to the relative merits of the many types of steels used in automobile construction.

J. H. G. M.

High Speed Steel. By MARCUS A. GROSSMAN and EDGAR C. BAIN. (New York : John Wiley & Sons, Inc. ; London : Chapman & Hall, Ltd. 1931. 17s. 6d. net.)

The addition of various alloying metals to steel produces in many cases astonishing effects on the properties of the latter ; in some cases indeed it would appear, at least to a casual observer, that the properties originally possessed by the steel had been completely changed. When manganese steel was discovered by Hadfield, for example, the discoverer when describing the new steel to the Iron and Steel Institute, especially commented on its abnormal behaviour on being quenched from high temperatures ; it was softened instead of hardened as would have been the case with ordinary steel.

High speed steel furnishes another example in which the alloyed steel seems to possess attributes quite foreign to those of the parent metal, though possibly the difference is not quite so striking as in the case of manganese steel. At the same time, a study of high speed steel, as of other alloy steels, indicates that its behaviour accords with certain fundamental principles deducible from the behaviour of ordinary carbon steels ; the mode of operation of these principles may be, and often is, modified by the alloying metals added to steel but the principles are still manifest. This, at least, is the firm opinion of the authors of this excellent book on high speed steel ; as a result, they have described the properties of the steel largely from this view point.

In speaking thus of high speed steel, it would appear as though this constituted but one alloy ; actually, of course, the term is used to include a number of tool steels which differ quite considerably in analysis but which exhibit surprising similarities in their structural characteristics and their response to various heat treatment processes. Probably the type most used is that containing about eighteen per cent. tungsten together with about four per cent. chromium and one per cent. vanadium and to this material, the authors devote most attention.

The first seventy-six pages of the book record what the authors consider to be good practice in the melting, casting, hot working, annealing, and hardening of high speed steel together with other operations—machining, grinding, inspection—incidental to the production of finished tools. These chapters contain much useful information, evidently garnered from the authors' close acquaintance with manufacturing conditions.

The second and somewhat longer part consists of an account of fundamental physical properties, constitutional diagrams, micro-structures developed by various manufacturing conditions and heat treatment processes and their correlation with ultimate mechanical properties. Here again one finds much useful information carefully analysed and clearly presented to the reader ; one finds also considerable originality of thought. In particular, attention should be drawn to the efforts of the authors to simplify the study of the constitution of these steels, bearing in mind their variableness in composition. While we are not sure that the subject admits of quite so much simplification as the authors suggest, we acknowledge very readily that the picture they present of the structural conditions existing in high speed steels of various compositions is a very interesting and helpful one and of considerable value to those wishing to probe further into the fundamental constitution of these steels.

Both the metallurgist and the manufacturer of high speed steel will find the book well worth reading and studying carefully ; to the engineer who is interested in the tools he uses, it may also be recommended as giving a straightforward and readable account of the manufacture, properties and constitution of one of the most remarkable metals he uses.

J. H. G. M.

CORRECTION TO THE NOTE ON ADSORPTION AND REFLECTION PROCESSES IN THE INTERACTION OF HYDROGEN AND METALS.¹

By K. F. BONHOEFFER UND A. FARKAS.

Received 13th June, 1932.

By the investigation of the *ortho-parahydrogen* conversion on hot wires, we found in the case of nickel a discontinuity in the temperature dependence curves both of the heat given up by the wire to the gas and of the catalysis. We thought this was due to a continuous change on the surface of the wire which we ascribed to the formation and decomposition of a surface hydride. Dr. Feussner (Hanau a/M) called our attention to the fact that an article by H. Busch² had described similar effects. According to Busch's explanation, the discontinuity in the amount of heat given up is only apparent and is due to the fact that, under certain experimental conditions, the temperature distribution along the wire ceases to be uniform and the wire assumes different temperatures along its length. We found that the effect described by us is explainable according to Busch and that the explanation originally proposed by us is not tenable. Our change of conception could not be included in the printing of the complete report of the meeting, it being only possible to eliminate the parts concerned in the reprints of our article.

¹ *Trans. Farad. Soc.*, **28**, 242, 1932.

² *Annalen d. Physik*, **64**, 401, 1921.

THE DIRECT TITRATION OF MAGNESIUM AND MANGANOUS SULPHATES USING FLUORESCIN AS AN ADSORPTION INDICATOR, AND THE EXTENSION OF THE METHOD TO THE DIRECT TITRATION OF OTHER SOLUBLE SULPHATES AND ALUMS.

By A. W. WELLINGS.

Received 1st April, 1932.

The use of adsorption indicators in Volumetric Analysis is at present only in its infancy. Fluorescein and eosin have been employed as adsorption indicators in the direct titration of soluble halides with silver nitrate, by Fajans¹ and his co-workers, and Kolthoff.² Kolthoff³ has also used metanil yellow in the direct titration of copper chloride.

¹ Fajans and Hassel, *Z. Elektrochem.*, **29**, 495, 1923. Fajans and Wolf, *Z. anorg. Chem.*, **137**, 221, 1924.

² Kolthoff and van Berk, *Z. anal. Chem.*, **70**, 369, 1927.

³ Kolthoff, *Z. anal. Chem.*, **71**, 235, 1927.

The use of these indicators depends on preferential adsorption of ions on the surface of colloid particles with a colour change at the "end-point" of the titration.

In this paper are presented the results of the author's researches on the direct titration of soluble sulphates using fluorescein as an adsorption indicator.

Barium chloride was first used as the precipitant, but, although many organic dyes were tried as indicators, no positive results were obtained. Barium hydroxide was then tried as the precipitant, and, although this method, at first, also seemed doomed to failure, it was found subsequently that two sulphates, magnesium sulphate and manganous sulphate, gave a very distinct colour change with fluorescein when titrated with barium hydroxide. The colour change may be represented thus :

yellow \rightarrow pink \rightarrow dark orange.

A quantitative examination was then made. One-tenth molar solutions of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{MnSO}_4 \cdot 5\text{H}_2\text{O}$ were prepared by weighing the required amounts of the purest analytical reagents, and dissolving in CO_2 free distilled water. Portions of 25 mls. of these solutions were then titrated with accurately standardised one-tenth molar barium hydroxide, 5 drops of a 1 per cent. solution of fluorescein in alcohol being added to the sulphate solution to serve as the adsorption indicator. On running in the barium hydroxide solution a pink colour was observed which disappeared on shaking ; the "end-point" was indicated by the persistence of the pink colour which is turned to a deep orange on shaking, due to the mixing of the two precipitates, namely, barium sulphate and the hydroxide of either magnesium or manganese. It is shown below that adsorption occurs on the surface of the hydroxide particles. The quantitative results of these experiments are given in Table I.

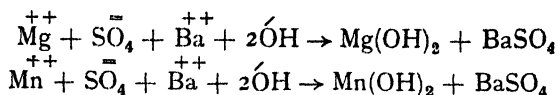
TABLE I.

	Mls. of 0.1M. $\text{Ba}(\text{OH})_2$ Equivalent to 25 Mls. of 0.1M. Solution of Hydrated Sulphate.	Concentration of the Hydrated Sulphate in Grams per Litre.	
		(a) By Titration.	(b) By Weighing.
$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$. .	25.0	24.6	24.640
$\text{MnSO}_4 \cdot 5\text{H}_2\text{O}$. .	24.9	24.0	24.100

It will be observed that the titration is a quantitative one. Satisfactory results were also obtained with one-twentieth molar solutions, but the colour change is hardly definite enough in weaker concentrations. Increase of temperature has little effect on the position of the "end-point."

Conditions for Accurate Titration.—The presence of traces of weak acids causes inaccurate results, since the first additions of barium hydroxide are employed in neutralising the acid. In the cases of strong acids such as hydrochloric and nitric the colour change is not observed even after neutralisation, unless they are present in very small amounts, since Cl^- and NO_3^- ions are preferentially adsorbed. On the other hand, the presence of OH^- ions does not materially affect the "end-point."

Mechanism of the Reaction.—In the reactions



two precipitates are produced. Since the colour change with fluorescein occurs only with these two sulphates, it is reasonable to suppose that the adsorption of ions occurs on the surface of the hydroxide and not on the barium sulphate, otherwise all sulphates should behave similarly. This may be confirmed by filtering the precipitates. The heavier barium sulphate tends to accumulate in the apex of the paper cone, while the lighter hydroxide which is coloured pink, is found on the sides of the cone; qualitative tests confirm this.

The explanation of the colour change is probably as follows: When a solution of magnesium or manganous sulphate is being titrated with barium hydroxide, with traces of fluorescein present, the anions of the fluorescein are not adsorbed by the colloid particles of the metallic hydroxide so long as sulphate ions are present in excess. When, however, all the sulphate ions have been removed as barium sulphate, the fluorescein anions are then adsorbed and change colour as soon as barium ions are also adsorbed. The colour change is therefore visible when there is one drop of the barium hydroxide solution in excess.

The Extension of the Method to the Direct Titration of other Soluble Sulphates and Alums.

Since the colour change with fluorescein described above occurs only on the colloid particles of manganous and magnesium hydroxides, it seemed possible that other sulphates could be titrated directly with barium hydroxide if particles of either of these hydroxides were present in the sulphate solution.

This was investigated in the first place by adding a milk of pure magnesium hydroxide to the sulphate solution, but, although fairly satisfactory results were obtained in some cases, the method was too cumbersome to be completely satisfactory. The most convenient method found was to add 5 mls. of 1 per cent. solution of crystalline manganous acetate to 25 mls. of 0.1 molar sulphate solution. The colour change with fluorescein then occurred on the surface of the colloid particles of manganous hydroxide formed in the titration with 0.1 molar barium hydroxide. A one per cent. solution of magnesium acetate was also found to be efficient. In some cases, particularly with ammonium sulphate, 1 ml. of the acetate solution was found to be sufficient, but, generally, 5 mls. was the minimum quantity found necessary for accurate titration.

In Table II. are given the experimental results of the titrations of a number of soluble sulphates and alums. The method of procedure was to prepare, by weighing the required amount of the purest analytical reagent or recrystallised salt and dissolving in CO_2 free distilled water, an accurate 0.1 molar solution of the salt. In preparing the standard solutions the formula weight was taken for convenience in each case; thus, the solution of cadmium sulphate actually corresponds to a 0.3 molar solution. The other exception was nickel ammonium sulphate, the limited solubility of which at room temperature necessitated the preparation of a 0.05 molar solution.

Five mls. of 1 per cent. manganous acetate and 5 drops of a 1 per

cent alcoholic solution of fluorescein were added to 25 mls. of sulphate solution, and the mixture titrated with 0.1 molar barium hydroxide solution. The barium hydroxide was carefully standardised before each separate determination. In the cases of those sulphates which are acid in solution owing to hydrolysis, *e.g.*, aluminium sulphate and the alums in particular, the solutions were first carefully neutralised with 0.1 normal ammonium hydroxide.

TABLE II.

Sulphate.	Mls. of 0.1 M. Ba(OH) ₂ Equivalent to 25 Mls. of Sulphate Solution.	Concentration of Sulphate in Grams. per Litre, Determined.	
		(a) By Titration.	(b) By Weighing.
(NH ₄) ₂ SO ₄	25.0	13.2	13.20
Na ₂ SO ₄	25.2	14.3	14.20
K ₂ SO ₄	24.7	17.2	17.43
Li ₂ SO ₄ . H ₂ O	24.9	12.7	12.79
ZnSO ₄ . 7H ₂ O	24.9	28.6	28.74
NiSO ₄ . 7H ₂ O	25.0	28.1	28.07
NiSO ₄ . (NH ₄) ₂ SO ₄ . 6H ₂ O	24.8	19.6	19.74
3CdSO ₄ . 8H ₂ O	74.9	76.8	76.94
Al ₂ (SO ₄) ₃ . 18H ₂ O	74.8	66.4	66.61
K ₂ SO ₄ . Al ₂ (SO ₄) ₃ . 24H ₂ O	99.7	94.6	94.85
(NH ₄) ₂ SO ₄ . Al ₂ (SO ₄) ₃ . 24H ₂ O	99.6	90.2	90.61

Here again the results are quantitative. It was found that, in this modification of the method, increase of temperature made the "end-point" uncertain and, in some cases, invisible; this was probably due to the solution of the small amounts of manganous hydroxide present in the solutions.

Negative results were obtained with the following sulphates, all of which form deeply coloured hydroxides thus masking the colour change: ferrous sulphate, ferrous ammonium sulphate, ferric sulphate, ferric alum, chromium sulphate, chrome alum, cobaltous sulphate, and copper sulphate. Curiously enough no difficulty was experienced with nickel sulphates. With the exception of the iron salts, the above substances gave the colour change in much diluter solutions than 0.1 molar, but the exact "end-point" was always difficult to determine.

Mercuric sulphate gave a very vivid colour change, but an exact estimation cannot be made owing to the precipitation of yellow basic mercuric sulphate during solution. From the results obtained it appeared probable that about 45 per cent. of the mercuric sulphate was precipitated as the basic salt at 10° C.

Summary.

Solutions of magnesium and manganous sulphates may be titrated directly with standard barium hydroxide solution, using fluorescein as an adsorption indicator. Other soluble sulphates which do not yield deeply coloured hydroxides may be titrated directly in the presence of magnesium or manganous acetates. The solutions of sulphates must be free from acid.

THE DIRECT TITRATION OF NORMAL OXALATES IN NEUTRAL SOLUTION USING FLUORESCIN AS AN ADSORPTION INDICATOR.

By A. W. WELLINGS.

Received 1st April, 1932.

Following the successful results obtained in the titration of soluble sulphates with barium hydroxide using fluorescein as an adsorption indicator, further experiments were performed in order to decide whether fluorescein could be employed similarly in other volumetric precipitation estimations.

It was found that, when neutral solutions of the three soluble normal oxalates were titrated with lead acetate solution in the presence of traces of fluorescein, a pink colour, which disappeared on shaking, was produced on the colloid particles of lead oxalate formed during the titration; the "end-point" of the titration was indicated by the persistence of the pink coloration.

One-tenth molar solutions of the lead acetate trihydrate, and of the monohydrated ammonium and potassium oxalates were prepared by weighing the required amounts of each pure analytical reagent and dissolving in air-free distilled water. The results were quantitative within the limits of experimental error.

The same oxalate solutions were then estimated by titration with standard potassium permanganate in the presence of sulphuric acid at 60° C. A solution of sodium oxalate was also determined volumetrically by both methods. The results of these determinations are given in the table; the two methods gave concordant results.

TABLE I.

Salt.	Mls. of Oxalate Solution Titrated.	Mls. of 0.1 M. Lead Acetate Required.	Mls. of 0.1 N. KMnO_4 Required.	Conc. in Grams per Litre of Anhydrous Oxalate.	
				(a) By Lead Acetate.	(b) By KMnO_4 .
$(\text{NH}_4)_2\text{C}_2\text{O}_4$.	25.0	24.9	49.7	12.35	12.32
$\text{K}_2\text{C}_2\text{O}_4$.	25.0	25.1	49.9	16.68	16.61
$\text{Na}_2\text{C}_2\text{O}_4$.	50.0	20.7	41.0	5.55	5.49

Conditions for Accurate Titration.—(1) The solutions must be neutral. No colour change occurs in acid solution; thus, the method is unsuitable for the titration of binoxalates and potassium quadroxalate. The presence of hydroxyl ions gives rise to a very vivid pink coloration, apparently due to preferential adsorption occurring on the particles of lead hydroxide formed in the titration. The "end-point" if alkali is present, is, therefore, bound to be inaccurate, as some of the lead

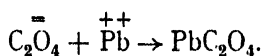
acetate is converted to hydroxide instead of a complete precipitation as oxalate.

(2) The colour change is quite satisfactory with solutions of one-twentieth molar concentrations, but it is inadvisable to employ concentrations weaker than this; the greater the concentration the more distinct is the colour change; as also, of course, is the liability of experimental error. One-twentieth or one-tenth molar concentrations are therefore the most suitable. The concentration of the indicator solution need not be so high as in the titration of sulphates; 5 drops of a 0.2 per cent. alcoholic solution of fluorescein are sufficient for from 25 to 50 mls. of oxalate solution. A little experience enables one to recognise the approach of the "end-point," as there is a distinct change in the state of aggregation of the precipitate.

(3) The lead acetate solution can be accurately standardised by means of a solution of normal oxalate, the molarity of which has been determined by titration with potassium permanganate in the usual manner. The lead acetate, however, must be run into the oxalate solution, and not vice versa, in order to obtain the colour change with fluorescein.

(4) Increase of temperature has little, if any, effect on the position of the "end-point." In fact, the colour change is slightly more distinct in warm solutions.

Probable Mechanism of the Colour Change.—The titration of the oxalate solution may be represented by the equation



Some of the oxalate ions are adsorbed on the colloid particles of lead oxalate, and, if traces of fluorescein are present, the anions of the dye-stuff are not adsorbed so long as oxalate ions are present in excess. When, however, all the oxalate ions have been removed as lead oxalate, the fluorescein anions are then adsorbed and change colour as soon as lead ions are also adsorbed. The colour change is therefore visible when there is one drop of the lead acetate solution in excess.

Summary.

Normal oxalates may be titrated directly, in neutral solution, by standard lead acetate solution, using fluorescein as an adsorption indicator. The titration may be performed at room temperature.

Leamington College.

THE LEAD-RICH ALLOYS OF THE SYSTEM LEAD-ANTIMONY EXAMINED THERMO- DYNAMICALLY.

By F. H. JEFFERY.

Received 11th April, 1932.

The technical importance of these lead-rich alloys justifies a further examination of their constitution.

It appears to have been definitely established that lead can hold antimony in solid solution and that the equilibrium diagram is probably of the Roozeboom type V. Dean, Hudson and Fogler¹ found that the maximum solubility of antimony in lead at the eutectic temperature was 2.45 per cent. Sb. They used "Doe-run" lead containing no determinable impurity, and Chinese antimony, this latter contained 0.107 per cent. S and 0.021 per cent. As. Schumacher and Bouton² found the solid solubility curve of antimony in lead, the solubility decreased continuously from its maximum 2.45 per cent. Sb at 247° C. to 0.24 per cent. Sb at 25° C. They used Bunker Hill lead containing 99.993 per cent. Pb and Kahlbaum antimony containing 99.97 per cent. Sb. They also gave a diagram of the lead-rich alloys of this series based on their own work and on the work of Dean, Zickrick and Nix,³ and of Schumacher and Nix.⁴ The question of the nature of the solid solution arises: the solute may be antimony or an inter-metallic compound of antimony and lead. The following thermodynamic analysis gives some evidence as to the constitution of the liquid and solid phases. The calculations are made from the results on which Schumacher and Bouton based their diagram.

When the simple assumption was made that the liquid phase was a solution of monatomic antimony molecules in monatomic lead molecules and that the solid solution in equilibrium with it had the same constitution, results were obtained which were quite at variance with the boundary conditions. It is found that these conditions can be satisfied if antimony combines with liquid lead to form the compound Pb_2Sb , the liquid phase being a solution of this compound in monatomic molecules of lead, and also if the corresponding solid phase is a solid solution of the compound Pb_2Sb in monatomic molecules of lead.

The thermodynamic equation is of the form:—

$$-\log(1 - n) + \log(1 - n') = \lambda/R\theta - \lambda/R\theta_0,$$

where n is the molal fraction of Pb_2Sb in the liquid phase and n' the molal fraction of Pb_2Sb in the solid phase, λ being sensibly constant throughout the range of temperatures and concentrations considered, provided the solutions are sufficiently dilute. Calculations are given for temperatures separated by intervals of five degrees and are continued until the concen-

¹ Dean, Hudson and Fogler, *J. Industrial and Engineering Chem.*, **17**, 1246, 1925.

² Schumacher and Bouton, *J. Amer. Chem. Soc.*, **49**, 1667, 1927.

³ Dean, Zickrick and Nix, *Trans. Amer. Inst. Mining Met. Eng.*, **73**, 505, 1926.

⁴ Schumacher and Nix, *Trans. Amer. Inst. Mining Met. Eng.*, **74**, 195, 1927.

trations become too large for the constancy of λ . The results are shown in the following table:—

θ .	Per Cent. Sb in Liquid.	Per Cent. Sb in Solid.	n .	n' .	$+\log(1-n)$ $-\log(1-n')$.	$1/\theta$.
600.4	—	—	—	—	0×10^{-3}	1.666×10^{-3}
598	0.50	0.15	0.87×10^{-2}	0.26×10^{-2}	2.66	1.672
593	1.20	0.45	2.14	0.78	6.00	1.686
588	1.80	0.75	3.26	1.32	8.62	1.701
583	2.35	1.00	4.33	1.77	11.46	1.715
578	3.00	1.25	5.63	2.23	15.38	1.730
573	3.65	1.50	6.99	2.70	19.58	1.745
568	4.40	1.65	8.62	2.98	26.01	1.761

Hence $-\log(1-n) + \log(1-n')$ is a linear function of $1/\theta$, the points lie on the straight line through the first and the seventh, the first point being given by $n = n' = 0$ and $\theta = \theta_0$ the freezing-point of pure lead. The calculations could not be carried further as the values of n become too large for dilute solutions.

The mean value of $\lambda = 1120$.

The constitutions of the liquid and solid solutions assumed are therefore justified. Inasmuch as the solid solubility curve is continuous down to 25°C . and has no "point saillant" below the eutectic isothermal it follows that the solid solution must have the composition Pb_2Sb in monatomic molecules of lead at all temperatures from the freezing-point of pure lead down to 25°C . This assumes that equilibrium has been obtained, which, according to Schumacher and Bouton, would have been almost impossible without the use of their method of severe cold-working by swaging.

Discussion of these Results.

1. Antimony combines directly with liquid lead to form the compound Pb_2Sb which dissolves in excess of the liquid lead.
2. The compound Pb_2Sb forms a solid solution in lead.
3. In the light of Benedicks' ideas the hardening effect produced by the addition of a small quantity of antimony to lead is probably due to the formation of this solid solution.
4. The existence of an intermetallic compound of lead and antimony has not been recognised in some recent investigations. Broniewski and Sliwowski⁵ found no evidence of definite compounds but found solid solutions of antimony in lead and of lead in antimony. Stephens⁶ examined the Hall effect, electrical resistivity, temperature coefficient of resistance and thermo-electric power of these alloys, and considered that his curves gave no evidence either of solid solutions or of compounds.
5. If the thermodynamic analysis as given by the author be correct the compound Pb_2Sb must maintain its identity in solid solution. Solomon and Jones⁷ examined these alloys by an X-ray method, using the alloys made and annealed by Stephens. They found no evidence that a compound exists.

This is another instance of the results of X-ray analysis being at variance

⁵ Broniewski and Sliwowski, *Revue de Met.*, **25**, 392, 1928.

⁶ Stephens, *Phil. Mag.*, **9**, 547, 1930.

⁷ Solomon and Jones, *Phil. Mag.*, **10**, 470, 1930.

with the result of the author's thermodynamic analysis as far as the existence of intermetallic compounds in a solid solution is concerned. None the less, the two methods seem to be equally justifiable by theoretic considerations.

The author would insist on the difficulty of obtaining equilibrium conditions in the solid state as is made clear by the work of Schumacher and Bouton.

*The Goldsmiths' Metallurgical Laboratory,
Cambridge.*

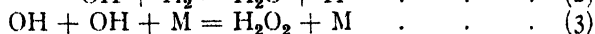
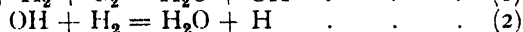
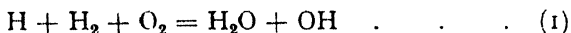
Contribution from the Frick Chemical Laboratory of Princeton University.

THE PHOTOCHEMICAL, MERCURY-SENSITISED REACTIONS BETWEEN HYDROGEN, OXYGEN AND CARBON MONOXIDE.

BY M. BARAK¹ AND HUGH S. TAYLOR.

Received 12th April, 1932.

In spite of numerous investigations of the mercury-sensitised reactions of hydrogen-oxygen mixtures,² there is still considerable speculation as to the precise mechanism of the process. The most recent paper on the subject² accepts the so-called Haber mechanism for the interaction of hydrogen atoms and hydrogen-oxygen mixtures in which a chain of processes



occurs, the second being important at elevated temperatures and thus leading to long chains with (3) obtaining in the neighbourhood of room temperatures. According to this mechanism the yield at ordinary temperatures should be at least 2 mols. of water for each mol. of peroxide, a result which Frankenburg and Klinkhardt found experimentally. Their results are, however, directly contrary to earlier work of Bates and Taylor³ who found, under favourable conditions, a product essentially 100 per cent. hydrogen peroxide. This result is quite incompatible with reaction (1) of the Haber mechanism, but it has been ignored by all who have thus far interested themselves in the mechanism in question. Marshall,⁴ also, in a separate investigation, using moist gases and a dynamic system, obtained peroxide formation which in the initial stages of his experiments was substantially pure peroxide though in the later stages of the reaction some of the peroxide formed was being decomposed. A yield of 1 mol. peroxide to 2 mols. water on the Haber mechanism also requires a 100 per cent. efficiency for reaction (3). There is no direct experimental evidence for such an efficiency. Indeed,

¹ Commonwealth Fund Fellow.

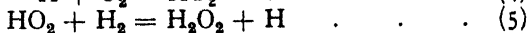
² For literature references, see Frankenburg and Klinkhardt, *Trans. Faraday Soc.*, **27**, 431, 1931.

³ Bates and Taylor, *J. Am. Chem. Soc.*, **49**, 2446, 1927.

⁴ Marshall, *J. Am. Chem. Soc.*, **49**, 2763, 1927.

the work of Bonhoeffer and Pearson,⁵ and earlier work,⁶ with electrolysis would indicate a low efficiency for such a reaction.

The alternative mechanism first put forward by one of us⁷ involved the formation of HO_2 and its subsequent reaction with molecular hydrogen to form hydrogen peroxide

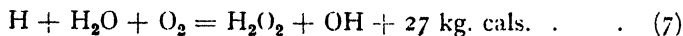


This would account for the Bates-Taylor and Marshall observations of pure peroxide formation and if the mechanism were correct, water would be formed as a decomposition product of the peroxide not as a primary product. Two objections have been urged against this mechanism. It has been pointed out that reaction (5) is endothermic to the extent of 31 kg. cal., whereas reaction (1) is 33 kg. cal. exothermic from which one might conclude that reaction (1), the Haber mechanism, would be preferred. The endothermicity of (5) is based on the assumption that the binding of two successive hydrogen atoms to an oxygen molecule involves a heat of reaction of 69 kg. cal. in each case. If, however, HO_2 were a kind of moloxide it is quite possible that its heats of formation would be markedly inferior to 69 kg. cal., and, as a consequence, the reaction (5) might even be exothermic. It may be pointed out that a combination of (4) and (5) gives



which process is overall exothermic. A word of caution may here be inserted against a tendency to use calorimetric data as a rough index to the occurrence of alternative reactions. Quantum mechanical studies⁸ have shown that strongly exothermic atom reactions may require large activation energies. More recent calculations of this type dealing with the hydrogen-chlorine combination,⁹ also indicate that reactions involving hydrogen atoms and $\text{H}_2 + \text{Cl}_2$ simultaneously require higher activation energies than the possible bimolecular processes $\text{H} + \text{Cl}_2$ and $\text{Cl} + \text{H}_2$.

The second objection to the HO_2 mechanism is based on the observation that it suggests a chain mechanism. Marshall's quantum efficiency measurements, 6.7 molecules of H_2O_2 per absorbed quantum have been questioned by Frankenburger and Klinkhardt, who find values between 1 and 2 (mean about 1.2) with the larger values obtained the more reliable. A value of 1 follows from the reactions (1) to (3). To account for values of 1.5-2 which these authors obtained they cite a possible reaction



which with reaction (3) for OH would yield a net of $3\text{H}_2\text{O}_2$ per absorbed quantum. In moist gases they suggest that this occurs to an extent of 25 per cent. in one of their experiments. This would mean, owing to the operation of the concentration factor, that reaction (7) was much more easily achieved than reaction (1), again an illustration of lack of correlation between exothermicity and ease of reaction.

It is evident that experimental work is thus far not adequate to

⁵ Bonhoeffer and Pearson, *Z. physik. Chem.*, **14B**, 1, 1931.

⁶ Traube, *Ber.*, **15**, 2434, 1882; Fischer and Priess, *ibid.*, **46**, 698, 1913.

⁷ Taylor, *Trans. Faraday Soc.*, **21**, 560, 1926. This mechanism is frequently referred to in the German literature as the *Marshall'sche Kette*.

⁸ Eyring, *J. Am. Chem. Soc.*, **53**, 2537, 1931.

⁹ Kimball, *Thesis*, Princeton, 1932.

permit decision between these various alternative mechanisms. A number of researches dealing with this reaction are at present in progress in Princeton. The present research records some further studies of a static $\text{H}_2\text{—O}_2\text{—Hg}$ system as well as of a system in which carbon monoxide was also present in order to ascertain the partition of oxidation between the two gases hydrogen and carbon monoxide.

Experimental.

Apparatus.—The experiments were carried out in the usual static system, consisting of a quartz reaction vessel, connected on one side to a constant volume mercury manometer by means of a quartz-to-pyrex graded seal, and on the other by a two-way stopcock to a vacuum line and gas reservoirs. Vacuum was obtained by means of a mercury diffusion pump backed up by a Cenco "High-Vac." oil pump.

Reaction Vessel.—An annular quartz vessel, length 10.5 cm., width 12 mm., was used and was kept in a constant temperature bath. The temperature of the bath was kept constant to about 0.2 of a degree by a continuous stream of water, variations in the actual temperature being obtained by passing the stream through heated lead coils. After two or three experiments, particularly those with excess of oxygen, small amounts of mercuric oxide were found to have accumulated in the reaction system. This was removed by filling the vessel with hydrogen and illuminating it with the cooled arc or by removing the vessel from the apparatus and cleaning with nitric acid and water.

Mercury Concentration.—The reaction was found to be very sensitive to the amount of mercury in the system. The preliminary measurements made with about 2 or 3 c.c. of mercury in the bottom of the vessel, gave results which were practically non-reproducible. The rate of reaction for any one mixture was always fastest for the first measurement made after the addition of fresh mercury and was slower for subsequent measurements when the mercury surface had become slightly tarnished with a film of oxide. A private communication from Marshall indicated that, under the conditions of his experiments, reproducible results were obtainable only when there was a large pool of mercury in the vessel and also a film condensed on the walls. Bates also found that the rate of reaction in a static system was greatly accelerated by increasing the amount of mercury in the reaction vessel. Later experiments carried out with a large pool of mercury in the vessel and a film on the outer wall gave a faster rate which was much more reproducible. Finally it was found that if the gases, before admission to the reaction chamber were passed over a pool of mercury heated to 70° or 80° C. and then over pools at room temperature, the reaction rate was approximately reproducible and these conditions were maintained for all the subsequent measurements. This latter rate was the fastest that could be obtained under the given conditions of experiment.

Arc.—The arc, which was of the vertical type, length 12 cm., diameter 2 cm., was placed co-axially within the annulus and was cooled to a height of 2 cm. above the mercury level by means of a stream of cold water. It was operated normally on 7.2 amps. of current and 20-22 volts of potential drop across the electrodes. Preliminary experiments with the arc run hot on 2.6 amps. and 70-75 volts showed no pressure change in a 2/1 mixture of hydrogen and oxygen.

Preparation of Gases.—Hydrogen, oxygen and stoichiometric 2/1

"electrolytic gas" were prepared by the electrolysis of 15 per cent. potassium hydroxide solution. Impurities in the oxygen and hydrogen were removed by passing the gases over heated platinised asbestos. The gases were then passed through sulphuric acid and over phosphorous pentoxide. Carbon monoxide was prepared by dropping strong sulphuric acid on to formic acid, the gas being bubbled through sulphuric acid and passed through a trap immersed in liquid air.

Procedure.—The course of the reaction was studied by noting the pressure indicated by the manometer at suitable intervals, usually one minute. Electrolytic gas was first examined and then measurements were made of the effect on the course of the reaction of excess of either constituent and also of carbon monoxide. For these latter experiments, about 300 mm. of electrolytic gas were taken in each case and the required excess of either gas to give the desired ratio. When it was required to make an analysis of the products of the reaction, a portion of the residual gases were removed by means of a Topley pump, being drawn through a trap immersed in a mixture of acetone and solid carbon dioxide where the non-volatile constituents were frozen out.

Analysis of Products.—This was carried out in a modified Bone and Wheeler gas analysis apparatus. Carbon dioxide was absorbed in 60 per cent. potassium hydroxide solution, oxygen in alkaline pyrogallol, carbon monoxide in ammoniacal cuprous chloride solution. Hydrogen was measured as residual gas.

Experimental Results.

(1) **Electrolytic Gas.**—Four experiments are included in Table I. to show the reproducibility of the results. In view of the variability and gradual deterioration of the arc, this is considered to be as good as can be expected. Column 6 of the table gives the average value of the four series and column 7, values for the pressure decrease during each minute.

It will be seen from the table that at room temperatures, 14° C., the rate of reaction was not constant, as Marshall had found it to be under similar arc conditions for temperatures between 50-70° C., but increased steadily, even after the first variation due to attainment of water vapour saturation, to the point corresponding to practically complete reaction. Marshall indicated something similar in his experiments at 25° C., at which temperature he had difficulty in obtaining reproducible results. In order to determine whether this increase in the rate was due to the accumulation of some autocatalyst in the reaction system, as had been observed by Bäckström¹⁰ in the case of the photochemical oxidation of benzaldehyde, the reaction was interrupted at various points by dropping a metal cylinder over the arc and shutting off the light for periods of five minutes. It was found that during the first minute of darkness there was a slight pressure decrease, less than 1 mm., and probably a temperature effect, but that for the remainder of the period of darkness the pressure in the system was steady. When the illumination was continued, the reaction rate did not begin *ab initio* but proceeded from the point at which it had stopped. Analyses of the products made after the reaction had proceeded more than half-way, when the reaction rate was increasing fairly rapidly, always gave

¹⁰ Bäckström, *Medd. K. Vetenskapsakad. Nobel Inst.*, 6, Nos. 13 and 16, 1927.

TABLE I.—ELECTROLYTIC GAS.

Series Initial Press. Temp. Time (mins.)	1. 296.5 mm. 14.0° C.	2. 297.6 mm. 14.8° C.	3. 302.8 mm. 14.4° C.	298.4 mm. 14.2° C.	Mean ΔP .	dP/dt .
	Decrease in Pressure in mm.					
1	2.6	1.7	2.6	3.2	2.5	2.5
2	13.2	9.9	11.8	10.9	11.5	9.0
3	23.0	20.8	22.8	21.2	22.0	10.5
4	33.8	31.0	32.9	32.0	32.4	10.4
5	45.1	41.9	43.4	43.4	43.5	11.1
6	55.3	52.2	54.6	54.7	54.2	10.7
7	67.1	63.6	65.8	66.5	65.8	11.6
8	78.3	74.9	77.4	79.4	77.5	11.7
9	91.7	86.5	90.1	91.8	90.0	12.5
10	103.5	99.2	101.8	104.4	102.2	12.2
11	115.7	111.4	116.0	114.2	114.3	12.1
12	129.2	123.5	129.2	125.3	126.8	12.5
13	141.7	136.8	142.8	137.3	139.7	12.9
14	154.9	149.8	157.8	150.7	153.3	13.6
15	167.7	163.9	172.9	164.9	167.4	14.1
16	181.6	178.0	186.9	180.4	181.7	14.3
17	194.7	192.6	202.7	195.7	196.4	14.7
18	208.3	207.6	218.4	210.9	211.3	14.9
19	221.7	219.6	233.1	226.4	225.7	14.4
20	235.2	233.8	248.4	242.4	240.0	14.3
21	247.4	247.0	263.8	257.8	254.0	14.0
22	259.0	259.6	276.4	271.0	266.5	12.5
23	268.2	271.3	287.5	280.5	276.9	10.4
24	274.7	282.4	290.9	283.0	282.9	5.9
25	276.9	286.4	291.0	—	—	1.0
26	277.6	—	—	—	—	—

TABLE II.—RATES OF REACTION FOR $3H_2 : 1O_2$ AND $4H_2 : 1O_2$ MIXTURES.

3 : 1 Mixture. 100 mm. H_2 ; 300 mm. Electrolytic Gas. T = 14° C.			4 : 1 Mixture. 205 mm. H_2 ; 308 mm. Electrolytic Gas. T = 12.7.	
Total ΔP mm.	dP/dt for Previous Min.	Time in Mins.	Total ΔP mm.	dP/dt for Previous Min.
0.9	0.9	1	1.5	1.5
3.1	2.2	2	3.0	1.5
15.7	4.0	5	13.0	3.3
44.1	5.9	10	33.5	5.0
74.6	6.7	15	56.8	5.0
108.2	7.1	20	85.0	6.0
145.7	8.1	25	116.0	6.6
187.9	8.8	30	152.0	7.5
235.5	10.3	35	193.0	9.0
283.5	8.0	40	238.0	9.0
289.5	2.0	42	257.5	10.3
291.5	1.0	44	278.8	10.5
292.0	0.3	46	298.5	8.5
—	—	48	201.9	1.7

a ratio of disappearance of hydrogen to oxygen of 2/1. Attempts were also made at these points to detect hydrogen peroxide, but no positive tests could be obtained either in the freezing trap to the gas analysis apparatus or in the reaction vessel itself. Variations in the initial pressure seemed to have very little effect, the curves for mixtures of various initial pressures being practically superposable.

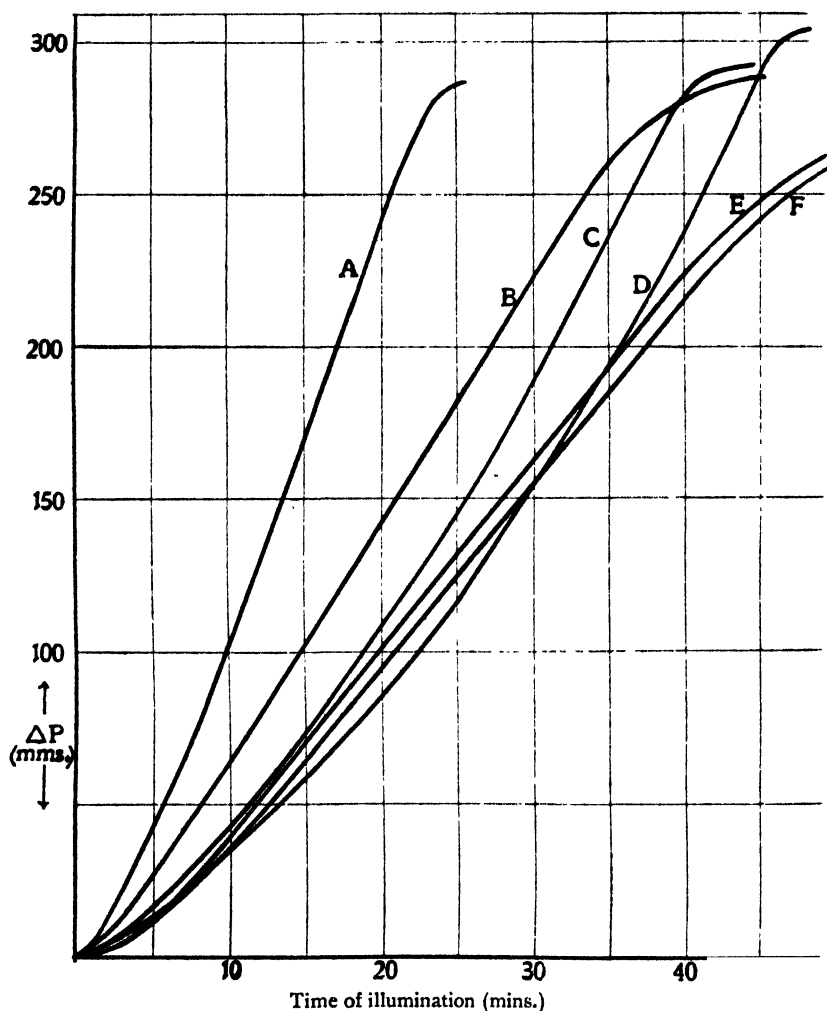


FIG. 1.—Relation between pressure change and time of illumination for hydrogen-oxygen mixtures.

A = H_2/O_2 , 2/1. B = 5/3. C = 3/1. D = 4/1. E = 4/3. F = 1/1.

(2) **Excess of Hydrogen.**—Table II. gives typical results obtained with mixtures containing ratios of hydrogen to oxygen of 3/1 and 4/1. Some fifty measurements with these mixtures show the same increase in rate as was found for the stoichiometric 2/1 mixture. These results are expressed graphically in Fig. 1 where the decrease in pressure is plotted against the time of illumination. It will be seen from the

graphs that the average rate of reaction, indicated by the slope of the pressure-time curves was greatest for the 2/1 mixture but that the increase in rate was greater for the 3/1 and 4/1 mixtures, as is shown by the increasing curvature of the reaction curves for these mixtures. Variations of ± 200 mm. in the initial pressure appeared to have no appreciable effect. In these experiments with excess of hydrogen, only the slightest traces of mercuric oxide were noticeable at the end of each measurement. Analysis of the products of a 4/1 mixture made after the reaction had gone more than half-way to completion, again gave a 2/1 rate of disappearance of the constituent gases and no trace of peroxide could be detected in the reaction vessel.

(3) **Excess of Oxygen.**—Table III. shows the effect of excess of oxygen.

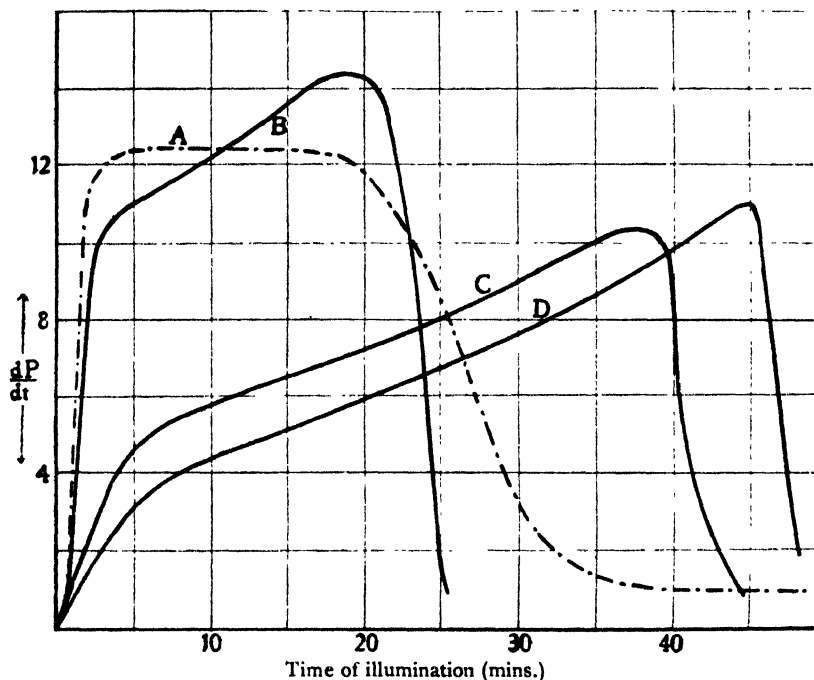


FIG. 2.—Relation between pressure change per minute and time of illumination. Hydrogen-rich mixtures.

A = carbon monoxide—electrolytic gas mixtures.
 B = H_2/O_2 , 2/1. C = 3/1. D = 4/1.

It will be seen from the table that the rate was approximately constant for the greater part of the reaction, decreasing towards the end when the oxygen concentration was becoming fairly large. This is apparent from Fig. 1 where the curves for mixtures containing excess of oxygen are approximately linear. As in the case of hydrogen, excess of oxygen caused a decrease in the rate of reaction of the stoichiometric 2/1 mixture, indicated by a decreasing steepness of slope as the proportion of oxygen increased. But the rate was found to be more sensitive to small traces of oxygen. Thus the decrease in rate caused by the addition of less than 20 mm. to the 2/1 mixture was almost two-thirds as great as that caused by the addition of 100 mm. of hydrogen. After an experiment

with excess of oxygen, the surface of the mercury and the outer wall of the reaction vessel were coated with a film of oxide.

Figs. 2 and 3 show the relation between dP/dt and time, smooth

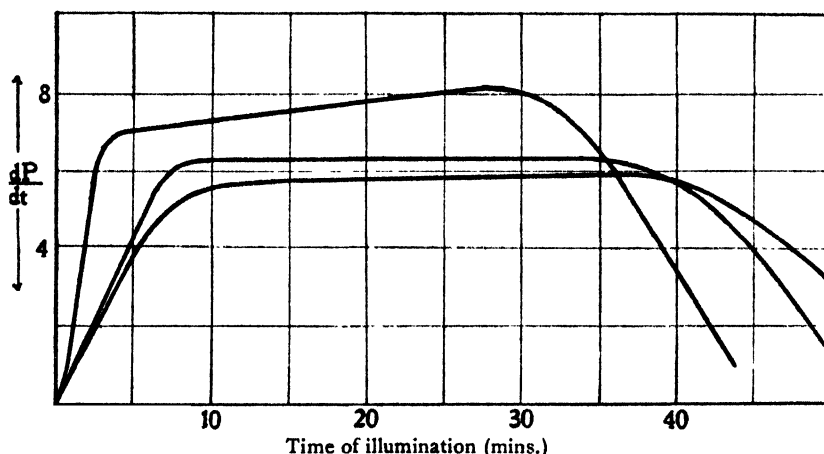


FIG. 3.—Relation between pressure change per minute and time of illumination. Oxygen-rich mixtures.

curves being drawn through the points for each gas mixture. It will be seen that while curves for mixtures containing excess of hydrogen exhibit a fairly steep slope and considerable curvature, those for mixtures containing excess of oxygen are practically linear and horizontal.

TABLE III.—RATES OF REACTION FOR OXYGEN-RICH MIXTURES.

Time in Mins.	5:3 Mixture. 16.8 mm. O_2 ; 303.4 mm. $2H_2 + O_2$ $T = 14.2^\circ$.		4:3 Mixture. 47.9 mm. O_2 ; 299 mm. $2H_2 + O_2$ $T = 14.4^\circ$.		1:1 Mixture. 99.1 mm. O_2 ; 292 mm. $2H_2 + O_2$ $T = 15.3^\circ$.	
	Total ΔP mm.	dP/dt for Previous Min.	Total ΔP mm.	dP/dt for Previous Min.	Total ΔP mm.	dP/dt for Previous Min.
1	1.9	1.9	1.2	1.2	1.2	1.2
2	5.9	4.0	2.6	1.4	2.5	1.3
5	26.5	7.0	11.8	4.2	10.2	4.0
10	63.5	7.1	38.8	5.0	37.2	5.6
15	101.6	7.7	70.3	6.9	64.9	5.4
20	140.9	7.4	102.0	5.5	93.0	6.2
25	181.0	7.6	133.3	6.2	123.2	6.2
30	221.9	8.0	163.8	5.8	153.3	5.9
35	260.1	7.2	192.6	5.8	184.8	6.6
40	280.6	2.3	222.5	5.7	216.0	6.2
45	285.3	0.5	247.5	4.0	242.0	4.9
50	—	—	265.5	3.0	260.8	3.0
55	—	—	275.5	1.0	272.9	1.6
60	—	—	278.5	0.9	277.4	1.1

(4) **Effect of Carbon Monoxide at Room Temperatures.**—Several measurements were made of the effect of different amounts of carbon monoxide on the course of the electrolytic gas reaction. The results for three of these experiments are given in Table IV. It will be seen

that the rate of reaction for these mixtures was approximately constant, the pressure-time curves, shown in Fig. 4, being practically linear. At a point corresponding to that at which all the oxygen had been used, the curves changed direction and again became approximately linear, the rate after this point corresponding roughly to the rate of reaction of hydrogen and CO alone (see Table V.). Variations in the amount of CO present appeared to have little effect on the reaction,

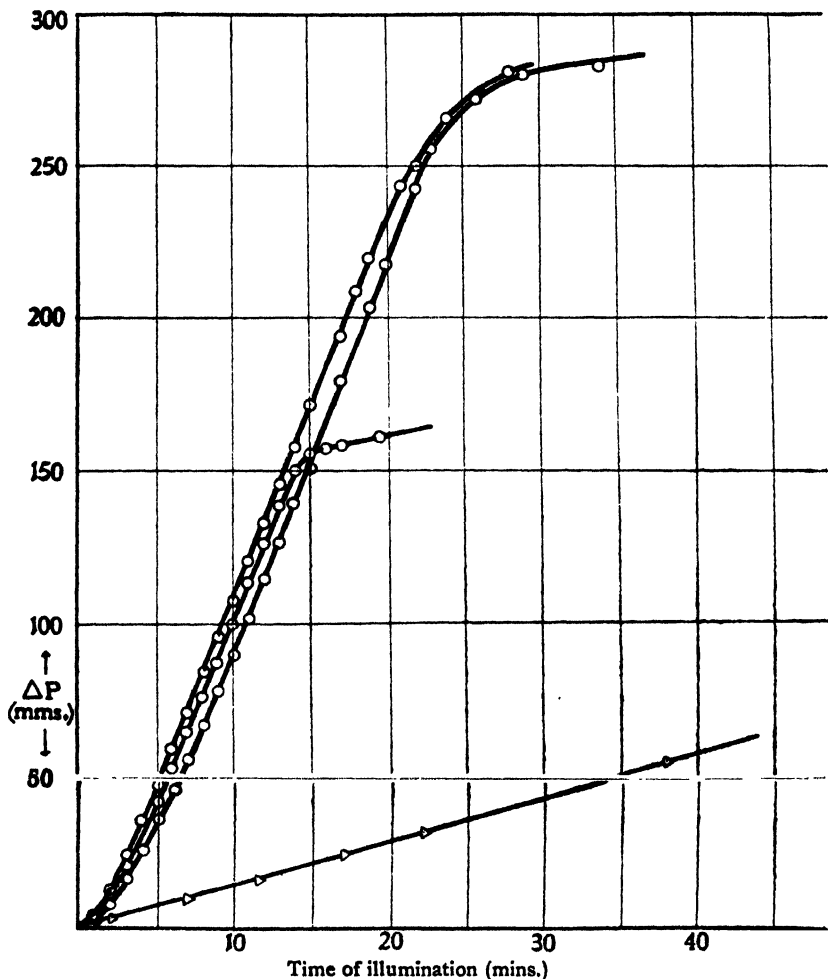


FIG. 4.—Relation between pressure change and time of illumination for carbon monoxide-electrolytic gas mixtures. (Δ carbon monoxide and hydrogen alone.)

the rate being the same for mixtures containing 25 per cent. and 40 per cent. of carbon monoxide. It will be seen from Fig. 2 that the rate of reaction of these mixtures was approximately the same as the average rate for electrolytic gas alone. Some of the experiments with carbon monoxide showed an induction period of varying length and this point will have to be established, but all the measurements gave linear pressure-time curves which were almost exactly parallel.

TABLE IV.—EFFECT OF CO.

Initial Press.	Series 1. Electr. Gas 185.7 mm. CO 58.3 Temp. 14.3° C.		2. 307.1 mm. 99.7 14.6° C.		3. 298.7 mm. 202.5 15.0° C.	
	ΔP mm.	dP/dt for Previous Min.	ΔP mm.	dP/dt for Previous Min.	ΔP mm.	dP/dt for Previous Min.
1	3.2	3.2	3.2	3.1	3.8	3.8
2	11.2	8.0	7.4	4.3	12.1	8.3
5	41.5	10.2	35.5	10.1	46.9	11.7
8	75.8	11.6	66.4	10.7	83.4	12.3
10	99.7	12.5	89.7	11.5	107.6	11.6
12	125.9	13.1	114.3	12.7	132.7	12.9
14	150.2	12.5	138.3	12.2	157.5	11.9
15	155.7	5.5	150.3	12.0	169.8	12.3
17	157.7	0.9	176.7	13.2	196.5	12.9
20	—	—	216.3	13.0	230.6	11.8
23	—	—	255.5	12.7	256.8	8.0
25	—	—	269.1	3.1	267.8	5.0
28	—	—	276.7	2.4	281.5	4.7
30	—	—	—	—	287.9	3.1
32	—	—	—	—	290.8	0.9

TABLE V.—REACTION BETWEEN H₂ AND CO.H₂, 202.5 mm.; CO, 200.6 mm. T = 14.4° C.

Time in Minutes.	ΔP mm.	dP/dt for Previous Min.
1	1.9	1.9
2	3.3	1.4
7	9.7	1.3
12	16.7	1.4
17	24.0	1.5
22	31.7	1.5
27	39.2	1.5
38	53.7	1.5
59	75.9	1.1
62	78.7	1.0
67	82.6	0.8
72	86.7	0.8

Several analyses were made of the products of the reaction at the point of inflexion of the curves, the reaction being stopped immediately after the rate had begun to decrease. Table VI. gives the results of two such series of determinations.

TABLE VI.

Series 1.				Series 2.		
Gas.	Initial Press. mm.	Final Press. mm.	Amount Used. mm.	Initial Press. mm.	Final Press. mm.	Amount Used. mm.
H ₂	196.8	27.5	169.3	201.2	32.1	169.1
O ₂	98.4	1.7	96.7	100.6	3.7	96.9
CO	104.3	80.0	24.3	200.9	168.2	32.7
CO ₂	—	23.7	—	—	26.7	—

Assuming that in series 1 all the CO formed CO_2 , the theoretical amount of oxygen used would be

$$\frac{169.3}{2} + \frac{23.7}{2} = 96.5 \text{ mm. (Amount measured} = 96.7.)$$

Series 2 gave a fairly strong positive test for formaldehyde, the reaction vessel being removed and washed with water and the wash water tested with Schiff's reagent. Assuming that the difference between the amounts of CO used and CO_2 formed represents the amount of formaldehyde formed, the theoretical amount of oxygen used would be

$$\frac{169.1 - 6.0}{2} + \frac{26.7}{2} = 95.0 \text{ mm. (Amount measured} = 96.9.)$$

These results are summarised in Table VII. which gives in column 2 the ratio of the amounts of hydrogen to carbon monoxide used in each case and in columns 3 and 4 the percentage of CO which reacted to form CO_2 and formaldehyde.

TABLE VII.

H_2/CO .		CO_2/CO Per Cent.	$\text{H}_2\text{CO}/\text{CO}$ Per Cent.
Initial Pressures.	Amounts Used.		
2/1	7/1	100 per cent.	—
1/1	5/1	80 per cent.	20 per cent.

(5) **Mercury-sensitised Reaction between Oxygen and Carbon Monoxide.**—Under exactly the same conditions which gave a rate of reaction of about 12 mm. per minute in the case of a mixture of electrolytic gas and carbon monoxide, a mixture containing 200 mm. of carbon monoxide and 100 mm. of oxygen gave a pressure decrease of 3.2 mm. in forty-eight minutes. The addition of a few drops of water to the reaction system caused a decrease in pressure of 13.3 mm. after seventy-one minutes. This latter rate corresponds to a value for dP/dt of 0.2 mm. per minute which is about 1/60th of that when hydrogen is present.

Discussion.

The above experimental facts may be briefly summarised as follows :—

(1) At about 14°C . and in a static system, mixtures rich in hydrogen showed an increase in rate as the reaction proceeded, the increase being more marked as the proportion of hydrogen in the mixture was increased. Analysis of the gas mixture during the reaction always gave a 2/1 ratio of disappearance of hydrogen to oxygen and no peroxide could be detected in the reaction system.

(2) The rate of reaction of mixtures rich in oxygen was approximately constant.

(3) The average rate of reaction was greatest for the 2/1 mixture and decreased as the proportion of either constituent was increased.

(4) Mixtures of electrolytic gas and carbon monoxide showed a constant rate of reaction which was approximately equal to that of

electrolytic gas alone. Between 80 and 100 per cent. of the carbon monoxide which reacted formed carbon dioxide.

(5) With equal concentrations of hydrogen and carbon monoxide in the same reaction mixture oxidation of the former is five times as rapid as the latter under the influence of excited mercury.

(6) The interaction of hydrogen and carbon monoxide occurs at approximately 18 per cent. of the rate ($-d[H_2]/dt$) for electrolytic gas or carbon monoxide-electrolytic gas mixtures under similar experimental conditions.

In dynamic systems the results of the researches in Princeton point unequivocally to the initial exclusive formation of hydrogen peroxide. This is true not only of the Bates-Taylor and Marshall experiments cited in the introduction but also of two independent sets of experiments using both hydrogen atoms from excited mercury and from a Wood's discharge tube which will be published elsewhere at a later date. We assume, therefore, that the water produced in the static experiments herein recorded is obtained via peroxide. The increase in rate with time observed in these static experiments and most marked in hydrogen-rich mixtures is definite evidence that the total reaction is accomplished in stages. The auto-acceleration observed reminds one of the same phenomenon observed in autooxidation reactions in which the intermediate existence of peroxides has been proved. This auto-acceleration is present even in the $2H_2 : 1O_2$ mixtures where there is no change in reaction gas composition, thus excluding the possibility of the acceleration being due to the changing ratio of reacting gases.

It is evident that this auto-acceleration is suppressed by increase of temperature, since Marshall did not observe it in the temperature range $50-70^\circ C.$, and also by increase of oxygen concentration. The secondary stages in the total reaction must, therefore, involve a small activation energy. The effect of oxygen which, in small concentrations causes an increase in total rate (up to $2H_2 : 1O_2$), must set up reactions which diminish the tendency to auto-acceleration. It is of interest in this connection to recall that the effect of oxygen concentration is similar in the thermal oxidation of a variety of hydrocarbons which are known to be chain processes. Thus, Spence and Kistiakowsky¹¹ found such an influence for acetylene-oxygen mixtures and that the maximum rate is obtained, as in our experiments, with mixtures of approximately constant composition irrespective of the total pressure. It is also to be noted that carbon monoxide exerts an influence similar to oxygen in suppressing auto-acceleration. This fact and the smallness of the yield of carbon dioxide in mixtures containing equal quantities of hydrogen and carbon monoxide is consistent also with a preliminary exclusive formation of hydrogen peroxide and a subsequent temperature-sensitive sequence of reactions.

The experiments cited provide decisive proof also that the oxidation process must involve short chains. The fact that hydrogen and carbon monoxide interact at approximately 18 per cent. of the rate ($-d[H_2]/dt$) for electrolytic gas or carbon-monoxide-electrolytic gas mixtures under similar experimental conditions indicates that the quantum yield in the two processes must be 18 : 100 or approximately 1 : 6. Such a result is quite incompatible with the quantum yield studies of Frankenburger, Klinkhardt, Steegerwald and Zimmermann on $H_2 + CO$ and Franken-

¹¹ Spence and Kistiakowsky, *J. Am. Chem. Soc.*, **52**, 4844, 1930.

burger and Klinkhardt¹² on $H_2 + O_2$. In both these sets of researches the quantum yield was approximately 1.15. If this value were correct for the formaldehyde reaction ($H_2 + CO$) our measurements would indicate a chain length of 6.9 for the oxidation process, a result which would conform to Marshall's earlier measurements and be in disagreement with the more recent studies in Frankenburger's laboratory. One would have then to explain the lowness of the latter results by decomposition of peroxide in the long arcs employed either by mercury or atomic hydrogen or else by assuming extensive hydrogen atom recombination without reaction with the low concentrations of oxygen used in the Frankenburger-Klinkhardt measurements.

There is one further possible explanation of the results obtained in this investigation by the static method. It may be that the bulk of the water is produced by the interaction of atomic hydrogen with mercuric oxide formed from the mercury in the system. The auto-acceleration would then be attributable to increasing amounts of oxide (not visible with hydrogen-rich mixtures) in the reaction zone. This would account for the large relative hydrogen oxidation as compared with carbon monoxide oxidation. Such a mechanism would not alter the conclusion with respect to chain length in the oxidation reaction. Indeed, it would imply even longer reaction chains. It is proposed to test these alternative proposals by further studies in flow systems.

Summary.

(1) In static systems, at 14° C., the reaction of hydrogen and oxygen under the influence of excited mercury shows an auto-acceleration when hydrogen-rich mixtures are employed.

(2) In mixtures rich in oxygen or containing carbon monoxide the rate of reaction is approximately constant.

(3) The average rate is a maximum for $2H_2 : 1O_2$ mixtures.

(4) With equal concentrations of hydrogen and carbon monoxide, oxidation of the former is five times as rapid as the latter under the influence of excited mercury.

(5) The interaction of hydrogen and carbon monoxide occurs at approximately 18 per cent. of the rate ($-d[H_2]/dt$) for electrolytic gas or carbon monoxide-electrolytic gas mixtures under similar experimental conditions.

(6) The data obtained are consistent with an initial substantially exclusive formation of hydrogen peroxide in oxygen containing mixtures and with a reaction sequence involving short chains having a mean chain length of approximately six.

One of the authors (M. B.) wishes to express his indebtedness to the Commonwealth Fund for the Fellowship which enabled this work to be carried out.

¹² Frankenburger and Klinkhardt, *Z. Elektrochem.*, **36**, 757, 1930.

THE INFLUENCE OF HIGH FREQUENCY CURRENTS ON POLARISED ELECTRODES.

PART I.

By S. GLASSTONE AND G. D. REYNOLDS.

Received 30th March, 1932.

The electrolytic detector for use in wireless telegraphy, involving a polarised point electrode (area approximately 3×10^{-6} sq. mm.), was described independently by Schloemilch¹ and by Fessenden.² The latter author considered that the operation of the detector was due to a decrease in the resistance at the electrode surface brought about by the heating effect of the high frequency oscillations, but this view was shown to be untenable by Reich,³ Rothmund and Lessing,⁴ and Ives.⁵ Schloemilch had stated that the electrolytic detector would only function when the polarised point electrode was made the anode, and in consequence Reich³ proposed a mechanism based on the observations of Ruer⁶ that low frequency alternating currents reduce the polarisation at a platinum anode; Rothmund and Lessing,⁴ however, showed that high frequency currents were able to influence the potential at a cathode as well as an anode. These authors observed that the effect of high frequency currents was negligible unless the electrodes used were polarisable; the oscillations apparently have a depolarising influence and permit an increased current to flow through a cell as a result of the reduction of back E.M.F. The explanation proposed to account for this depolarisation was based on the assumption that the potential of a polarised electrode is able to respond immediately to the rapid variations of current; although this may be the case with low frequency alternating currents,⁷ it is probably not so when, as for the oscillations under discussion, the alternations are at the rate of about a million per second (*vide infra*). Bennewitz⁸ concluded from observations on a platinum anode in sulphuric acid that high frequency oscillations reduce the minimum overvoltage, but the values quoted are unreliable as they were obtained from supposed "break points" in current-voltage curves. Bancroft⁹ considered that electric waves reduce overvoltage because an electrical stress tends to remove adsorbed gas; this cannot be the only factor responsible for the influence of high frequency currents, since these currents have a marked effect in the presence of depolarisers when the electrode potential is much below that at which gas evolution would normally occur. Cooper¹⁰ has made a limited number of observations on the increase of

¹ *Elektrotechn. Z.*, **24**, 959, 1903.

² *Elec. World and Engineer*, Sept. 19, 1903; see *Elektrotechn. Z.*, **24**, 1015, 1903.

³ *Physikal. Z.*, **5**, 338, 1904.

⁴ *Ann. Physik*, **15**, 193, 1904.

⁵ *Physikal. Z.*, **11**, 1181, 1910.

⁶ *Z. physikal. Chem.*, **44**, 81, 1903.

⁷ Jones, *Trans. Amer. Electrochem. Soc.*, **41**, 151, 1922.

⁸ *Z. physikal. Chem.*, **72**, 202, 1910; see especially p. 223.

⁹ *Trans. Amer. Electrochem. Soc.*, **29**, 309, 1916; see also *J. Physic. Chem.*, **29**, 20, 1925.

¹⁰ *Trans. Faraday Soc.*, **18**, 102, 1922; see p. 108.

direct current passing through a polarised cell as a result of the application of high frequency oscillations, but these do not appear to contribute towards the solution of the problem of the origin of the effect.

In reviewing previous work on the influence of high frequency currents on polarised electrodes it is clear that no satisfactory explanation of the depolarisation effect has yet been proposed, and so further investigation has been undertaken, especially as it appeared possible that such a study might throw light on the general problem of overvoltage.

Previous workers in this field had all used an induction coil with a spark gap as a source of high frequency oscillations; such an arrangement gives an unsteady output of "damped waves" of ever varying intensity. In the present work a thermionic valve oscillator was used to produce undamped oscillations of constant amplitude and frequency, and capable of control and measurement. Several oscillators were designed in the course of the preliminary work, and the one finally adopted has the advantage of a high frequency output of 1.5 watts and permits of the variation of the strength of the oscillating current without any appreciable change of its frequency. The actual frequency was determined by means of a standardised wave-meter, and the current strength measured by Ferranti "thermo-junction" milliammeters. Experiments showed that within the limits studied, 0.1 to 2×10^6 cycles per sec., the effect of the high frequency oscillations was almost independent of their frequency; a constant frequency of 10^6 cycles was therefore used in the present work.

Experimental.

The Oscillator.—For all but the preliminary work the apparatus represented in Fig. 1 was used as the source of high frequency oscillations; the whole of the current for the operation of the oscillator was obtained from the 200 volt A.C. electric light mains. The output was controlled by altering the resistance R_1 and thus varying the voltage applied to the anodes of the valves. The circuit was so designed that automatic adjustment of the grid-bias voltage occurred as the anode voltage was varied, and hence the valves were always maintained under correct operating conditions. The variable resistance R_2 , which served in this connection, was set at the commencement to give the anode current recommended by the makers of the valves, and was not altered during the course of the work. The frequency of the oscillations was adjusted by means of the variable condenser C_1 , and the output circuit was brought into resonance with the high frequency circuit by the aid of the condenser C_2 ; the arrangement of the output circuit is such as to prevent any A.C. or D.C. from the oscillator being superimposed on the high frequency currents.

Polarising Circuit.—The source of the polarising current was a 28-volts battery of large accumulators, the current strength being controlled by a variable high resistance (0.1 to 4 megohms) placed in series with the battery. The use of a high voltage and a high resistance avoids the difficulty experienced by Rothmund and Lessing⁴ of simultaneous variation in the polarising current and the electrode potential on the application of the high frequency oscillations.

Electrodes, Cell and Electrolytes.—Previous workers agree in stating that the depolarising effect of high frequency oscillations is only observed with very small ("point") electrodes, and consequently such

- I. *N*-sulphuric acid. p_H 0.
- II. *N*-acetic acid and *N*-ammonium acetate. p_H 4.6.
- III. 0.5 *N*-ammonium acetate, 0.25 *M*-potassium dihydrogen phosphate, and 0.25 *M*-disodium hydrogen phosphate. p_H 6.8.
- IV. *N*-ammonium hydroxide and *N*-ammonium acetate. p_H 9.4.
- V. 0.1 *N*-sodium hydroxide. p_H 13.

In addition to the platinum electrodes already described a number of experiments were also made with a lead electrode.

The Application of High Frequency Current to the Polarised Electrode.—One terminal of the high frequency output circuit (Fig. 1, $M_1M_2L_3C_2$) was connected to the test electrode and the other to a subsidiary electrode consisting of a spiral with ten turns of 24 S.W.G. platinum wire and having an overall diameter of 1.2 cm. and a length of 2.5 cm. The test electrode was situated centrally with respect to the spiral (Fig. 2). With this arrangement there was no possibility of the polarising current entering the high frequency circuit, on account of the high resistance of the condenser C_2 (Fig. 1) to direct current; further the leakage of high frequency current into the polarising circuit could only have been very small owing to the relatively high resistance of the electrolyte in the syphon tube and of the variable resistance used for controlling the polarising current. The strengths of the high frequency and polarising currents could thus be read on suitable meters independently of one another.

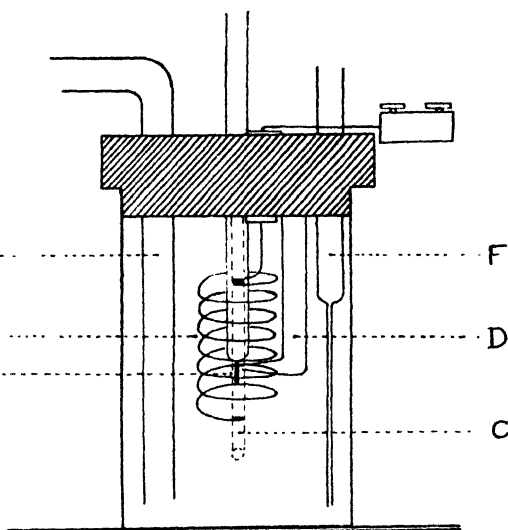


FIG. 2.

- A = test electrode.
- B = "high frequency" spiral electrode.
- C = glass support for spiral.
- D = Luggin capillary.
- E = syphon to other electrode compartment.
- F = tube for passing in gas.

Measurement of Electrode Potentials.—Before being set up for measurement the platinum electrodes were cleaned in concentrated nitric acid, followed by hydrochloric acid and then water; the lead electrodes were cleaned with dilute nitric acid and water only. The potential of the test electrode under various conditions was measured by combination with a standard calomel electrode containing saturated potassium chloride solution, connection between the two electrodes being made with a syphon tube. One end of this tube was drawn out into a fine tip, and inserted between two adjacent turns of the spiral (high frequency) electrode so as to press against the test electrode; close contact was ensured by the use of a spring outside the cell. The

E.M.F. of the calomel-test electrode combination was measured by the Poggendorf method using two resistance boxes (total 11,100 ohms) as a bridge, and a pointer galvanometer as null instrument. All potentials quoted in this paper are on the normal hydrogen scale, and all measurements were made at room temperature (about 17°).

Results of Preliminary Observations.—In the course of preliminary experiments with nickel, nichrome, platinum and lead electrodes it became evident that more reproducible results could be obtained when the electrode exposed to the high frequency oscillations was the cathode than if it were used as anode; consequently in the major portion of the work now described the test electrode was the cathode of the polarised cell. In order to make the results obtained for different electrodes, and even for the same electrode under different conditions, comparable with one another it was found necessary to polarise the cathode for a definite period with a current of one milliamp. before commencing to take potential measurements. Subsequently the electrode was allowed to remain under the influence of the desired high frequency and polarising currents for a few minutes in order that the potential might become reasonably steady.

The High Frequency Effect.—In the early stages of the present work the polarising current-cathode potential curves were plotted for each electrode with and without the application of high frequency oscillations. It became evident, as Rothmund and Lessing⁴ had suggested, that the reduction of electrode potential at a given polarising current density, resulting from the application of a given high frequency current, was very much greater at low polarising C.D.'s, before the formation of bubbles had commenced, than at high C.D.'s when gas was being liberated freely. It was necessary, therefore, to study the effect of high frequency currents—called for the sake of brevity the "H.F. effect"—under these two conditions, *viz.*, at high and low polarising C.D.'s, as well as to determine the influence, if any, of the high frequency currents on the minimum overvoltage, that is the overvoltage at which bubbles commence to be evolved from the electrode.

Electrode Size.—Before describing the results obtained in this study it is desirable to report a number of observations of general importance

TABLE I.—VARIATION OF THE H.F. EFFECT WITH THE APPLIED HIGH FREQUENCY CURRENT.

High Frequency Current. (milliamps.)	High Frequency C.D. (milliamps./mm. ²).	H.F. Effect (Volt.)
150	27.3	0.064
120	22.2	0.045
90	16.4	0.027
60	11.1	0.014
30	5.5	0.011
20	3.6	0.003
10	1.8	0.001

mately linear manner as the high frequency current was increased.¹¹

¹¹ The relationship between the H.F. effect and the magnitude of the current has been established more rigidly by experiments in the presence of depolarisers; the results of this work will be reported later.

A typical set of results is given in Table I.; this was obtained for a platinum cathode of 5.5 sq. mm. area, in *N*-sulphuric acid saturated with nitrogen, polarised with a direct current of 5 milliamps. per sq. dm. It cannot be maintained that these results are exactly reproducible, but there is no doubt whatever about their general tendency.

Rothmund and Lessing⁴ found that an electrode of the order of 2 sq. mm. in area showed no H.F. effect, and so it appears that in their experiments the maximum high frequency current passing through the cell was only a few milliamps. In view of the arrangement used for generating and applying the high frequency oscillations this is not at all improbable.

Another factor, which accounted for the fact that previous workers on the influence of high frequency currents on polarisation had found it necessary to use very small point electrodes, was brought to light in the preliminary work. It was observed that if the H.F. effect was expressed in relation to the high frequency current *density*, under a given set of conditions, the effect was found to be almost independent of the size of the electrode. It is evident, therefore, that the only particular virtue possessed by the point electrode used in the electrolytic detector is that it enables a reasonably large high frequency current density to be obtained; this explanation appears to have been suspected by Rothmund and Lessing.⁴ In Table II are quoted some results showing the relationship between the H.F. effect and the area of a platinum cathode for a given high frequency current of 150 milliamps.; the electrolyte was *N*-sulphuric acid and the polarising current density 250 milliamps. per sq. dm. in each case.

In view of the difficulty in obtaining exactly reproducible values of the

TABLE II.—H.F. EFFECT AND ELECTRODE AREA.

Area in Sq. Mm.	H.F. Effect.	Area \times Effect $\times 10^3$
0.9	0.24	216
1.7	0.11	187
3.9	0.04	156
8.8	0.03	264
16.1	0.013	209
34.0	0.005	170

H.F. effect and of measuring the areas of the small electrodes, it seems that the product of the H.F. effect and the area may be regarded as constant. The effect is thus inversely proportional to the area of the electrode for a given high frequency current strength; combining this conclusion with the one already drawn from results of the type quoted in Table I. it follows that the H.F. effect is approximately proportional to the high frequency current *density*, in a given electrolyte.

H.F. Effect at High Polarising C.D.—Since the preliminary work had indicated, and later experiments confirmed, the dependence of the H.F. effect on the electrode area, the more detailed work now to be described was performed on one electrode of platinum (6.5 sq. mm. area) and one of lead (12 sq. mm. apparent area) which had been roughened by use as a cathode. The polarising current at 1.1 milliamps. was applied for one hour before readings were taken in each solution and for each gas used; the gas (air, oxygen, hydrogen or nitrogen) was kept passing through the cell during the whole of this time and also whilst measurements were being made. After measuring the potential of the test electrode the high frequency oscillations were switched on at their maximum value and the electrode potential again determined. The intensity of the high frequency current was then adjusted to the nearest

multiple of 50 milliamps. and reduced in stages of 50 to zero, the potential being measured at each stage; from these measurements the H.F. effect at each value of high frequency current was determined. The results are not exactly reproducible, but there is no doubt concerning the general conclusions to be drawn from the figures quoted in Table III.; the actual potential of the electrode is given in the column headed " E ," whereas ΔE , the H.F. effect, is the reduction of cathodic potential resulting from the application of 150 milliamps. of high frequency current. For the platinum electrode the values of ΔE quoted are half the measured values, and so are equivalent to those for an electrode of about 13 sq. mm.; the results are thus comparable with those given for the lead electrode (12 sq. mm.).

TABLE III.—H.F. EFFECT AT HIGH POLARISING C.D.

Solution.	Gas.	Platinum Electrode		Lead Electrode	
		E .	ΔE .	E .	ΔE .
I. p_H 0	Air . .	— 0.348	0.011	— 0.999	0.004
	Oxygen .	— 0.368	0.026	— 0.965	0.005
	Hydrogen .	— 0.370	0.011	— 1.011	0.004
	Nitrogen .	— 0.332	0.016	— 1.007	0.003
II. p_H 4.6	Air . .	— 0.668	0.029	— 1.178	0.009
	Oxygen .	— 0.553	0.039	— 1.166	0.016
	Hydrogen .	— 0.623	0.024	— 1.200	0.013
	Nitrogen .	— 0.557	0.023	— 1.167	0.013
III. p_H 6.8	Air . .	— 0.754	0.044	— 1.192	0.021
	Oxygen .	— 0.765	0.048	—	—
	Hydrogen .	— 0.695	0.048	— 1.165	0.021
	Nitrogen .	— 0.808	0.039	— 1.156	0.021
IV. p_H 9.4	Air . .	— 0.801	0.032	— 1.526	0.016
	Oxygen .	— 0.767	0.036	—	—
	Hydrogen .	— 0.834	0.037	— 1.544	0.016
	Nitrogen .	— 0.795	0.040	— 1.503	0.016
V. p_H 13	Air . .	— 1.049	0.064	— 1.801	0.025
	Oxygen .	— 1.024	0.080	—	—
	Hydrogen .	— 1.041	0.065	— 1.807	0.022
	Nitrogen .	— 1.024	0.061	— 1.823	0.022

An examination of Table III. shows that the H.F. effect on potential is small at high polarising currents and almost independent of the gas passed into the electrolyte; similar results were obtained with other values of high frequency current and need not be reproduced here. A comparison of corresponding values for platinum and lead electrodes indicates that the H.F. effect is somewhat greater with cathodes of the former metal; in view of subsequent results it is doubtful if this difference is at all significant for the present problem, and is probably connected to some extent with slight differences in the slopes of the current-potential curves for the two metals.

The irregular variation of the H.F. effect with changes in the hydrogen ion concentration of the electrolyte in the polarised cell was at first very perplexing; it will be noted that with both platinum and lead cathodes as the p_H increases the magnitude of the effect appears first

to increase, then to decrease, and finally to increase again. The similarity of the behaviour for the two electrodes suggested that a definite significance must be attached to the variation. It appeared at first that the nature of the ions present in the electrolyte had an influence on the H.F. effect, and in order to test this possibility various salts, which did not affect the hydrogen ion concentration, were added to solution II. (p_H 4.6), and the H.F. effect re-determined. The results obtained with 150 milliamps. of high frequency current at a platinum cathode are given in Table IV.

TABLE IV.—INFLUENCE OF SALTS ON THE H.F. EFFECT.

Salt Added.	H.F. Effect.	
	1.0 N.	0.5 N.
None . . .	0.033	0.033
Na ₂ SO ₄ . . .	0.031	0.033
NaCl . . .	0.023	0.025
KH ₂ PO ₄ . . .	0.023	0.028

The results in Table IV. are not sufficiently distinctive to indicate a specific influence of ions, but it is quite evident that added salts show a definite tendency to reduce the H.F. effect at a given high frequency C.D.

H.F. Effect and E.M.F.—In the course of subsequent work it became evident that the variation of the H.F. effect with the nature of the solution was related to the different high-frequency E.M.F.'s which must be applied across the cell in order to produce a given C.D. at the point electrode. The value of the alternating E.M.F. (e) for a given solution and point electrode was determined by measuring the heat developed in the solution on passing a known high frequency current for a known time. Since the output circuit used contained both capacity and inductance and was "tuned," it is probable that the phase angle of the alternations is zero, and consequently the energy liberated by a current h in time t is equal to eht , in the appropriate units; the value of e may thus be determined. The cathode portion of the experimental cell was well wrapped with cotton wool and placed in a Dewar vessel, which was itself enclosed in a wooden box packed with cotton and felt. A gentle stream of nitrogen passing through the cell kept the electrolyte stirred. The high frequency current was applied and the temperature of the electrolyte was read off at regular intervals in order to determine the rate of heating; a correction was applied for heat losses by means of a cooling curve taken when the high frequency current was off. The heat capacity of the glass vessel and of the electrodes was neglected in comparison with that of the electrolyte. In Table V. are given the values of the high frequency E.M.F. (e) required to produce a current of 150 milliamps. with test electrodes of about 13 sq. mm. area, and the corresponding H.F. effects (ΔE) taken from Table III.; the parallelism is shown by the values of $e/\Delta E$.

It appears from these results that the variation of the H.F. effect is probably due only to the differences in the high frequency E.M.F. required to pass a given current through the various electrolytes. The E.M.F. depends principally on the electrical resistance of the solutions, and so it is not surprising to find that the H.F. effect in 0.1 *N*-sodium hydroxide is several times greater than in *N*-sulphuric acid. The

addition of salts to the electrolyte increases the conductance and so decreases the E.M.F. required and hence the H.F. effect; the results quoted in Table IV. are thus readily explained.

TABLE V.—COMPARISON OF H.F. EFFECT AND APPLIED E.M.F.

Solution.	Platinum.			Lead.		
	e .	ΔE .	$e/\Delta E$.	e .	ΔE .	$e/\Delta E$.
I. . . .	0.30	0.011	27	0.30	0.004	75
II. . . .	1.00	0.029	34	1.00	0.009	111
III. . . .	1.08	0.044	25	1.08	0.021	52
IV. . . .	0.93	0.032	29	0.93	0.016	58
V. . . .	2.25	0.064	35	2.25	0.025	90

H.F. Effect at Low Polarising C.D. The preliminary treatment of the electrode consisted in the application of the 1 milliamp. polarising current for thirty minutes followed by another thirty minutes at a C.D. just below that at which experiment (*vide infra*) had shown bubbles of hydrogen ceased to be evolved. The high frequency current was then applied and measurements taken in the same manner as for the high polarising current. Some of the results obtained, with a high frequency current of 150 milliams., in the course of a large number of observations are given in Table VI.

TABLE VI.—H.F. EFFECT AT LOW POLARISING C.D.

Solution.	Gas.	Platinum.		Lead.	
		E .	ΔE .	E .	ΔE .
I.	Air . . .	— 0.031	0.109	— 0.540	0.255
	Oxygen . .	— 0.030	0.211	—	—
	Hydrogen .	— 0.032	0.004	—	—
	Nitrogen .	— 0.030	0.006	—	—
II.	Air . . .	— 0.277	0.395	— 0.999	0.376
	Oxygen . .	— 0.333	0.470	— 0.878	0.562
	Hydrogen .	— 0.290	0.009	— 0.907	0.032
	Nitrogen .	— 0.337	0.026	— 0.909	0.028
III.	Air . . .	— 0.421	0.510	—	—
	Oxygen . .	— 0.425	0.487	—	—
	Hydrogen .	— 0.433	0.034	—	—
	Nitrogen .	— 0.434	0.025	—	—
IV.	Air . . .	— 0.574	0.429	— 1.022	0.642
	Oxygen . .	— 0.580	0.418	—	—
	Hydrogen .	— 0.592	0.019	— 1.097	0.027
	Nitrogen .	— 0.599	0.030	— 1.098	0.018
V.	Air . . .	— 0.738	0.900	— 1.329	0.815
	Oxygen . .	— 0.752	0.795	—	—
	Hydrogen .	— 0.782	0.030	— 1.383	0.083
	Nitrogen .	— 0.784	0.046	— 1.431	0.036

The H.F. effect with small polarising currents is evidently no longer independent of the nature of the gas with which the electrolyte is saturated; the effect is very small with hydrogen or nitrogen, and exceptionally large when air or oxygen is present. The variation of the effect with the nature of the electrolyte is very similar to that with high polarising currents, and there seems little doubt that this is related to the fall of high frequency E.M.F. across the cell. The proportionality of the H.F. effect and E.M.F. is, however, not quite so definite as with high polarising currents, since there is a limit set to the magnitude of the effect at low polarising C.D.'s; this limit is determined by the "standing" or "resting" potential of the electrode in the absence of any current. For example, a lead electrode polarised at low C.D. in *N*-sulphuric acid has a cathode potential of -0.54 volt.; on application of 100 milliamps. of high frequency current this was reduced to -0.30 , whereas 150 milliamps. reduced the potential to -0.285 and 200 milliamps. to -0.280 volt. The potential of an unpolarised lead electrode in *N*-sulphuric acid is -0.28 volt approximately. It is clear, therefore, that the high frequency current is unable to reduce the potential of the cathode below the "resting" value, and consequently the maximum H.F. effect in *N*-sulphuric acid is $0.54 - 0.28 = 0.26$ volt; similar limitations to the H.F. effect are to be found in other electrolytes both with lead and platinum electrodes. It may be emphasised here that the inability of the high frequency oscillations to change the potential of an electrode from its resting value is a very strong argument against the theory of Rothmund and Lessing.⁴

H.F. Effect on Minimum Overvoltage.—For the minimum overvoltage measurements both lead (12 sq. mm.) and platinum (6.5 sq. mm.) electrodes were used, the former being roughened somewhat by preliminary use as a cathode. Before commencing to make a measurement of overvoltage a polarising current of 1 milliamp. was passed through the cell for thirty minutes; the current was then reduced rapidly to 400 microamps. and more slowly until close to the point at which gas bubbles ceased to be evolved. After each alteration in the value of the current a period of two minutes was allowed to elapse and the electrode then observed during a further minute for the liberation of gas bubbles; if no bubbles were seen to leave the electrode during this period the evolution was said just to have ceased. From the potential of the electrode measured in this condition the minimum overvoltage was calculated. The visual observation was checked by noting the point at which a break occurred in the potential/log. current curve. In every case the value of the current at which hydrogen bubbles just ceased to be evolved, that is the so-called "residual current," was also noted. The minimum overvoltage and residual current measurements were made both with and without the applied high frequency oscillations; the results obtained under a variety of conditions are given in Table VII.

The figures in Table VII. show that although the value of the minimum overvoltage varies somewhat, probably owing to the difficulties of measurement with such small electrodes as had to be used in the present work, no definite tendency can be observed. On the whole the results lead to the conclusion that high frequency oscillations have no appreciable influence on the minimum overvoltage for hydrogen evolution; this appears to be the case both for a low (platinum) and for a high (lead) overvoltage metal. The suggestion made by Bennewitz⁸ that high frequency currents decrease polarisation by reducing the minimum

TABLE VII.—MINIMUM OVERVOLTAGE AND RESIDUAL CURRENT.

Solution.	H.F. Current.	Air.	Oxygen.	Hydrogen.	Nitrogen.
<i>Overvoltages Platinum Electrode.</i>					
I. . . .	None	0.04	0.05	0.03	0.05
	200 m.a.	0.03	0.04	0.03	0.05
II. . . .	None	0.05	0.06	0.03	0.06
	210 m.a.	0.02	0.04	0.02	0.05
III. . . .	None	0.04	0.06	0.04	0.03
	132 m.a.	0.03	0.10	0.03	0.03
IV. . . .	None	0.05	0.03	0.05	0.04
	215 m.a.	0.04	0.02	0.03	0.02
V. . . .	None	0.03	0.04	—	0.04
	150 m.a.	0.03	0.01	—	0.04
<i>Residual Currents in Microamps.</i>					
I. . . .	None	9	30	1.6	6
	200 m.a.	14	56	1.8	8
II. . . .	None	13	31	1.9	2.1
	210 m.a.	23	55	2.9	2.9
III. . . .	None	18	38	10	9
	132 m.a.	28	100	10	26
IV. . . .	None	25	50	12	12
	215 m.a.	92	92	26	14
V. . . .	None	27	50	—	18
	150 m.a.	51	100	—	24
<i>Overvoltages—Lead Electrode.</i>					
I. . . .	None	0.60	—	—	—
	250 m.a.	0.66	—	—	—
II. . . .	None	0.68	0.59	0.69	0.64
	235 m.a.	0.68	0.63	0.68	0.61
III. . . .	None	0.63	—	—	0.60
	225 m.a.	0.53	—	—	0.60
IV. . . .	None	0.54	—	0.56	—
	227 m.a.	0.59	—	0.58	—
V. . . .	None	0.67	—	0.70	—
	165 m.a.	0.77	—	0.64	—
<i>Residual Currents in Microamps.</i>					
I. . . .	None	14	—	—	—
	250 m.a.	21	—	—	—
II. . . .	None	25	57	12	12
	235 m.a.	47	113	20	14
III. . . .	None	60	—	—	26
	225 m.a.	75	—	—	50
IV. . . .	None	13	—	5.6	—
	227 m.a.	23	—	6.7	—
V. . . .	None	20	—	2.4	—
	165 m.a.	36	—	3.3	—

overvoltage seems, therefore, to be improbable. Apart from the immediate problem it is of interest to note that the minimum cathodic overvoltage, both for lead and platinum, appears to be independent of the hydrogen ion concentration of the electrolyte and of the nature of the gas with which the solution is saturated. This result would seem to establish the minimum (bubble) overvoltage as a definite property of

an electrode, in spite of a recent tendency for it to be ignored or its significance denied.¹²

Residual Current and the H.F. Effect.—A study of the residual current results given in Table VII. reveals the fact that the high frequency oscillations in general tend to cause an increase in this current at any particular electrode under a given set of conditions. The increase is much greater in the presence of air or oxygen than it is when the electrolyte is saturated with hydrogen or nitrogen. (It should be mentioned that some of the residual current values may not be quite reliable on account of the slight stirring effect resulting from the passage through the electrolyte of the gas with which it was being kept saturated; the results with and without high frequency oscillations are, however, comparable in every case as the measurements were made, as far as possible, under identical conditions.)

The residual current is generally regarded as a measure of the maximum amount of hydrogen which can be removed from a cathode by diffusion and by reaction with a depolariser; the polarising current must be at least equal to the residual current value before hydrogen can accumulate at the electrode and be evolved in the form of bubbles. Since high frequency oscillations have been found to increase the residual current, it is clear that their application results in an increased rate of removal of active material from the electrode by the process of diffusion or of depolarisation or by both. The increase of residual current is much greater in the presence of depolarisers, *viz.*, air and oxygen, than when no depolariser is present, and so it might appear that the high frequency oscillations increase the rate of depolarisation at the electrode, that is the rate of reaction between hydrogen and oxygen in the instances under discussion. The oscillations, however, undoubtedly have an influence even in the absence of depolarisers, and although the actual increase in the residual current is small the *relative* increase is in most cases quite appreciable. It must be concluded, therefore, that the high frequency oscillations increase the rate of removal of hydrogen from the electrode by both processes—diffusion and depolarisation; the increase in the latter could be brought about by an increase in the velocity constant of the reaction occurring at the electrode, but both processes would be accelerated by an increase in the rate of diffusion of gas to and from the cathode. The enhanced rate of diffusion *from* the cathode would be effective in increasing the residual current when a depolariser was absent, whereas both more rapid diffusion of hydrogen from, and of oxygen to, the electrode would be operative in the presence of the depolariser. The larger effect of the high frequency oscillations under the latter conditions can thus be explained. The increase in the diffusion rate can be brought about either by an increase in the diffusion coefficients of the gases or by a decrease in the thickness of the "diffusion layer"¹³ at the electrode, or by both changes occurring at the same time.

Discussion.

It appears that the increase of diffusion rate is sufficient to account for many of the observed effects of high frequency currents on a polarised

¹² Baars, *Brit. Chem. Abs.*, A. 423, 1930; Baars and Kayser, *Z. Electrochem.*, 36, 429, 1930.

¹³ Glasstone, *The Electrochemistry of Solutions*, 1930, p. 364.

electrode. At high polarising currents the rate of removal of hydrogen from the electrode in the form of bubbles is quite large and any further slight increase resulting from the increased rate of diffusion caused by the application of high frequency oscillations can only result in a small decrease of polarisation. The H.F. effect on potential at high polarising currents might therefore be expected, as it is found, to be small. As is to be anticipated also, the nature of the gas with which the electrolyte is saturated will have very little influence, although a slightly larger H.F. effect in the presence of oxygen is not surprising. It must be remembered that the solution in the vicinity of a cathode from which gas is being evolved freely will in any case be almost saturated with hydrogen; this fact may be partly responsible for the independence of the H.F. effect of the nature of the gas being passed into the electrolyte.

At low polarising currents, before gas bubbles commence to be evolved from the electrode, the situation is very different from that at high current densities, especially when a depolariser is present. The rate of liberation of hydrogen by the current is now less than the maximum rate of removal from the electrode, and any increase in the latter rate will cause a marked decrease in the amount of hydrogen which can accumulate at the electrode, and consequently in the cathode potential. The difference between the H.F. effect at low and high polarising currents is parallel to the effect of a small decrease in the actual polarising current under these conditions; an examination of the usual potential-current curve, with an almost horizontal portion becoming almost vertical at the potential of gas evolution, shows that at low polarising current a change in the latter produces a marked effect on the potential, but at high polarising currents a corresponding change will produce a negligible alteration.

The results in Table VII. show that the residual current in the absence of a depolariser and without applied high frequency oscillations is of the order of 5 to 10 microamps., for the platinum electrode used, whereas in the presence of oxygen the value is 30 to 50 microamps.; more hydrogen can therefore be removed by depolarisation than by diffusion. It is consequently not surprising to find, as already mentioned, that in the presence of air or oxygen the potential of a cathode at low polarising currents can be reduced to the resting value by the application of high frequency oscillations; the increased rate of diffusion of oxygen to the cathode results in the removal of almost the whole of the accumulated hydrogen. The H.F. effect on the potential under these conditions must, therefore, be large.

The very small effect of high frequency currents in the absence of a depolariser, at low polarising currents, leads to the conclusion that actually very little gas is lost from the electrode by diffusion; this is in agreement with the low residual currents, of the order of 2 microamps., found in some cases (see Table VII.), and it is not improbable that the higher values, of the order of 10 microamps., may be due to the entry of air or to unusual stirring by the saturating gas. There is no doubt, however, that a certain amount of gas can escape from the electrode by diffusion, and as the high frequency currents are apparently able to increase this rate of diffusion a decrease of potential due to applied high frequency oscillations is to be expected even in the absence of a depolariser; such an effect, although small, is certainly observed, as may be seen from an examination of Table VI. Since the "resting" potentials of the electrodes used in the present work are not reversible

potentials they will be influenced by the nature of the gases present in the electrolyte; these potentials will consequently be more positive when the solution is saturated with air or oxygen than when hydrogen or nitrogen is present. The *maximum possible* H.F. effect in the former instances must, therefore, be definitely greater than in the latter; this factor must be taken into consideration when comparing the effects at low polarising currents in the presence and absence of depolarisers.

The Electrolytic Detector.

The results of the work described in the present paper allow of an explanation of the mechanism of the electrolytic detector at one time used in wireless telegraphy. A polarised cell is in equilibrium and permits only a small current to flow, the magnitude of which depends on the rate of removal of gas from the electrode; this steady current can produce no sound in a telephone earpiece through which it passes. The incidence of high frequency oscillations, however, causes an increased removal of gas by diffusion, and possibly also by depolarisation, so that there is a sudden increase in the current flowing and a corresponding "click" is produced in the telephone receiver. In practice with the electrolytic detector it was customary to use a very small electrode just dipping into the surface of the electrolyte; this small area of contact served the dual purpose of providing a large high frequency C.D., and of permitting access of depolariser (air) to the electrode when it was a cathode. Both of these factors tend to increase the magnitude of the H.F. effect. With the point electrode as anode the depolarisation effect does not arise, but it is probable that the arrangement of the electrode at the surface of the solution permits an increased rate of diffusion of oxygen from the electrode when the high frequency oscillations are applied.

H.F. Effect at an Anode.—In order to obtain information concerning the effects of high frequency currents on anode potentials, some experiments were made with a platinum electrode of 6.5 sq. mm. exposed area, immersed to a depth of 3.4 cm. in *N*-sulphuric acid. The electrode was polarised for a short time as an anode and its potential measured at a series of decreasing C.D.'s both with and without applied high frequency oscillations; the H.F. effect on the potential was found to be about 0.016 volt for 150 milliamps. of high frequency current at all polarising C.D.'s other than the very smallest. This value is of the same order as that found for the same electrode when used as a cathode in *N*-sulphuric acid under similar conditions (Table III.). On repeating the observations with an electrode made of a longer wire but only immersed to an extent of 6.5 sq. mm. the H.F. effect at the anode had increased to about 0.05 volt. This enhanced effect is probably due to the increased rate at which the solution supersaturated with oxygen in the vicinity of the electrode can get rid of the excess to the atmosphere, as compared with an electrode which is immersed to an appreciable depth in the electrolyte.

It has been shown already that the H.F. effect at a cathode is proportional to the fall of high frequency potential across the cell; if the same factor is operative at the anode the effect should be greater in 0.1 *N*-sulphuric acid than in a *N*-solution. For an immersed 6.5 sq. mm. electrode the H.F. effect in 0.1 *N*-sulphuric acid was found to be about 0.06 volt for 150 milliamps. high frequency current; this, as expected,

is greater than the value in *N*-sulphuric acid. For an electrode at the surface the effect was only slightly greater, namely 0.065 volt; it is not surprising to find that when the H.F. effect is already large the further influence of the more rapid diffusion at the surface is relatively small.

The experiments just described, made with a platinum anode, were carried out in a solution originally saturated with air, and measurements were made to determine the effect of saturating the solution with hydrogen. At high polarising C.D.'s the H.F. effect was very little different from that in the air-saturated solution; at the very lowest polarising C.D.'s the electrode behaved as a hydrogen electrode and the H.F. effect was almost zero, but at C.D.'s just below that at which evolution of oxygen bubbles commenced the H.F. effect was greater than 0.3 volt. These results are similar to those observed for a cathode, and there is consequently no reason to suppose that the H.F. effect, or its mechanism, is different at anode and cathode; further confirmation for this view has been obtained in subsequent work.

Summary.

(1) The decrease of polarisation of an electrode resulting from the application of high frequency currents (called the H.F. effect) has been found to be approximately proportional to the high frequency C.D.

(2) At high polarising C.D.'s the H.F. effect is small and almost independent of the nature of the gas saturating the electrolyte; the magnitude of the effect, for a given high frequency C.D., appears to be proportional to the fall of high frequency E.M.F. across the cell.

(3) At low polarising C.D.'s the H.F. effect is very large in solutions saturated with air or oxygen but small in the presence of hydrogen or nitrogen; the effect, although limited by the resting potential of the electrode, appears to be related to the high frequency E.M.F.

(4) The minimum hydrogen overvoltage at platinum and lead cathodes has been measured under a variety of conditions; it has been observed that although the high frequency oscillations do not affect the minimum overvoltage they markedly affect the value of the residual current, especially in the presence of depolarisers.

(5) The H.F. effects on polarised electrodes and the mechanism of the "electrolytic detector" are accounted for on the basis of the assumption that the depolarising influence of high frequency currents is due to their causing an increase in the rate of diffusion of active material from, and of depolariser to, the electrode.

(6) It appears that the magnitude and mechanism of the H.F. effect is the same at both anode and cathode.

*The University,
Sheffield.*

NOTE ON THE ELECTRIC CHARGE ON AN OIL DROPLET IN AN EMULSION.

By W. C. M. LEWIS.

Received 4th March, 1932.

Experience has shown that at a hydrocarbon or other oil-water interface the oil carries a negative charge. The effect is ascribed to preferential adsorption of "primary" ions, employing Mukherjee's¹ term. Further there is evidence that the oil interface has already attained its equilibrium or limiting charge when only very small amounts of electrolyte are present.

In an emulsion of an oil dispersed in water the oil droplets apparently tend to attain a certain size distribution, the majority lying within relatively restricted limits. This is particularly the case when the emulsion is produced in what may be called the "synthetic" manner by dissolving a small quantity of oil in the minimum quantity of alcohol or acetone and pouring the mixture into water. It was pointed out by the writer² that the order of size thus obtained for the oil droplets was comparable with that which could be obtained by disintegration of the same quantity of oil in bulk, thus indicating a tendency to attain a critical size or range of sizes. As is well known emulsions prepared by disintegration methods possess a size distribution varying with the conditions of preparation, *cf.* for example Sibree.³ In view of this we shall confine our attention in the present instance to emulsions produced by the "synthetic" method. Using this method, Tuorila⁴ has prepared paraffin oil emulsions and has determined, by direct counting, the number of droplets present in a given volume of emulsion, whence, knowing the quantity of oil present, the mean radius can be obtained. Tuorila thus finds the value 0.72μ . He points out that the system is polydisperse containing some particles with radius as large as 10μ and also some below 0.1μ . A repetition of the writer's original measurements (in which direct readings are made with a high-power microscope) has been carried out in this Laboratory by Dr. James Pace. Using oils such as liquid paraffin, and purified olive oil in water alone and in water containing very dilute ($0.001 N$) potassium chloride, alkali, or sodium oleate, the majority of the droplets were found to have diameters lying between 1μ and 0.5μ . A number of larger particles were likewise present, but the range of sizes referred to appears to predominate. Thus, if, for the purpose of characterising the emulsion, we are to ascribe a single value to the mean equilibrium radius a_0 , we would set a_0 equal to 0.4μ . On this basis we shall ultimately attempt to calculate an average or mean charge. This charge will vary with the size of any actual droplet present, the charge density being taken to be a constant in view of the adsorption mechanism ascribed to the origin of the charge.

¹ Mukherjee, *Trans. Faraday Soc.*, **16**, Appendix, p. 163, 1920-21.

² Lewis, *Kolloid Z.*, **4**, 211, 1909.

³ Sibree, *Trans. Faraday Soc.*, **27**, 161, 1931.

⁴ Tuorila *Kolloid Z. Beihefte*, **27**, 44, 1928.

The existence of a size distribution lying within relatively small limits so far as the majority of the droplets is concerned suggests a balance between inwardly and outwardly directed forces. The case of the charged soap bubble (*cf.* Lodge⁵), and the case of charged water droplets suspended in water vapour (*cf.* J. J. Thomson⁶), in which an inwardly directed force due to surface tension is balanced by an outwardly directed force due to electric charge, suggests the application of similar considerations in the case of the droplets in an emulsion. In applying such considerations however to this case we have to take into account the existence of ions in the field surrounding the droplets and giving rise to the well-known electrical double layer distribution at the oil-water interface. This has been pointed out by L. F. Knapp⁷ who has deduced an expression connecting charge and size with the aid of energy considerations. Whilst accepting Knapp's treatment in principle it is worth while to consider in somewhat greater detail *that aspect of the problem which is concerned with the process of building up the droplets.* For the treatment outlined here the writer is greatly indebted to his colleague Professor Joseph Proudman, F.R.S.

In the first place the drop increases in size by accretion of smaller oil units. In view of the conditions of preparation these "smaller units" may well be uncharged oil molecules, *i.e.* units which may be said to possess zero energy in respect of electrical charge and surface (capillary) tension. The assumption that oil in the form of molecules adds itself to an aggregation of molecules (or an ultramicroton) carrying a charge q permits us to assume that, *during the process of growth*, q can be regarded as constant. Some such mode of increasing the mass or volume of the ultramicroton whilst the charge thereon remains constant must be postulated in order to render valid the treatment which is based on the consideration that some critical size will be eventually attained when the total free energy term of the growing droplet (made up as it is of the sum of an electrical energy term and an ordinary surface energy term) reaches a minimum. In general if δE_0 be the energy of type referred to (*viz.* electrical + capillary) possessed by one of the "smaller" units which are capable of being added to the charged ultramicroton, and if by such addition the energy of the ultramicroton be increased by δE , then the condition for increase in size is $\delta E < \delta E_0$, the condition for decrease in size being $\delta E > \delta E_0$, the condition for stationary size being $\delta E = \delta E_0$. It is only when δE_0 is zero (as it would be for an uncharged molecule of oil or an uncharged unit to which surface properties could not be ascribed) that we can make use of the criterion, $\delta E = 0$, for the attainment of a limiting or critical size on the part of the charged droplet itself.

From the definition of the energy term E of the charged droplet we can write

$$E = \frac{1}{2}q^2 \int_a^{a+d} \frac{dr}{Kr^2} + 4\pi a^2 \sigma \quad . \quad . \quad . \quad (1)$$

where q is the charge on the droplet, a the radius of the droplet, d the thickness of the electrical double layer around the droplet, K the dielectric capacity throughout the double layer, and σ the interfacial tension oil-water.

⁵ Lodge, "Modern Views of Electricity," 3rd Ed., p. 437, 1907.

⁶ Thomson, J. J., "Conduction of Electricity through Gases," 3rd Ed., Vol. I., p. 325, 1928.

⁷ Knapp, L. F., *Trans. Faraday Soc.*, 17, 457, 1921.

In order that the above expression may attain a minimum value at some stage of growth it is evident that the electrical term must decrease with increase in the radius a , since the capillary term $4\pi a^2\sigma$ obviously increases steadily with increase in a . The possibility of a decrease in the electrical term depends upon our regarding q as constant during the growth process, for if q were to increase as a increases it is clear that the electrical term would likewise increase (with a constant dielectric capacity) and no size limit would be theoretically attainable.* This constancy in q during the growth does not mean however that when the growth process is completed that droplets (of different size) will possess the same value of q . Droplets might be regarded as differing in size because they have originated from ultramicros which possessed different q values initially. The difference in size ultimately obtained in the stable emulsion is due to the attainment of a constant charge density independent of the size, each size adjusting itself, so to speak, to its own q in order to render q/a^2 the same for all the droplets.

Initially when the first clustering of oil molecules is taking place to produce ultramicros it is not improbable that the adsorption of OH^- ions will be a statistical effect so that the clusters will have different q values. Clearly the presence of a charge on a cluster will be a factor opposing further addition of charge, and it seems likely that it is this circumstance which permits of the attainment of a range of sizes in the equilibrated system which is not very wide. If a growing ultramicro happens to pick up an additional charge it will necessarily tend to grow to a larger final limit than would have been necessary in the first instance in order to arrive at a critical charge density.

Referring to equation (1) and assuming that the dielectric capacity K is constant throughout the electrical double layer, equation (1) may be written

$$E = \frac{1}{2} \frac{q^2}{K} \left(\frac{1}{a} - \frac{1}{a+d} \right) + 4\pi a^2 \sigma \quad (2)$$

Treating the interfacial tension as independent of curvature, which is probably correct for droplets of the size encountered in emulsion systems, it follows that

$$\frac{dE}{da} = \frac{1}{2} \frac{q^2}{K} \left(-\frac{1}{a^2} + \frac{1}{(a+d)^2} \right) + 8\pi a \sigma.$$

Hence the criterion

$$\frac{dE}{da} = 0,$$

gives the relation

$$\frac{q^2}{8\pi K} \left(\frac{1}{a^4} - \frac{1}{a^2(a+d)^2} \right) = \frac{2\sigma}{a} \quad (3)$$

If the thickness of the double layer is small compared with the radius of the droplet, and this is always the case for droplets of the size contemplated, it follows that

$$\frac{q^2}{4\pi K} \cdot \frac{d}{a^5} = \frac{2\sigma}{a} \quad (4)$$

or

$$q^2 = \frac{8\pi K \sigma a^4}{d} \quad (4a)$$

* It follows that we are limiting ourselves to those cases in which the charge is due to adsorption of ions from the surroundings. The case of structural ionisation met with in the proteins for example lies outside our present considerations.

or, denoting the charge density by ρ

$$\rho^2 = \frac{K\sigma}{2\pi d} \quad (4b)$$

Expressions (4), (4a) and (4b) have in effect been deduced by Knapp.

It will be observed that the terms on the dexter side of the equation (4b) are independent of the size of the droplets. Hence the charge density is the same for droplets of different size. This is the condition which one would expect to obtain on the basis of an adsorptive mechanism for the charge.

It may be pointed out that the above equations do not require that a *single* critical size shall be obtained. All that is required is that the size shall adjust itself to the charge already upon it to give a constant charge density.

It will be observed that in the above equations the dielectric constant has been taken as constant. The constancy of the dielectric capacity in turn requires that the double electrical layer shall be very thin, *i.e.* of the order of one molecular diameter, for one may expect in general that K would tend to rise rapidly over a range corresponding to a relatively small number (say 10) molecular diameters. It seems a reasonable inference from this that those balancing ions which are located at a position such as 10 molecular diameters distance from the core, *i.e.* at a position where the dielectric capacity is definitely different from that in the immediate neighbourhood of the core or oil surface, must be very few in number compared with the total number of balancing ions situated very close to the oil surface. In other words any effect depending upon ions located at a position, *i.e.* having a "centre of gravity," somewhat distant from the charged surface, must be of the nature of a residual effect. Since distance from the core would go hand-in-hand with mobility in an external electric field this suggests that electrophoretic phenomena are essentially "residual" effects.

We may now proceed to use equations (4a) and (4b) to calculate q and ρ in the case of the oil emulsion. In applying these equations the most suitable case to consider will be that in which sufficient electrolyte has been added to cause the double layer to consist completely of the rigid "limiting" type, *i.e.* the particle does not move in an electric field. Under these conditions it is usual to regard the thickness of the double layer as corresponding to the diameter of a single water molecule, *viz.* 3×10^{-8} cm. according to the estimate of Gouy.⁸ We shall denote this limiting thickness by d_0 . Setting $K = K_0 = 7$, the limiting value estimated by Rideal⁹ for the layer of water molecules at the surface of discontinuity and setting $\sigma = 50$ dynes per cm. (an average value for the interfacial tension between hydrocarbon oil and water) and $a = 4 \times 10^{-5}$ cm. it follows from equations (4a) and (4b) that

$$q = 8.5 \times 10^{-4} \text{ e.s.u.}$$

and the charge density

$$\rho = 4.3 \times 10^4 \text{ e.s.u.}$$

As already pointed out this value for q or ρ is regarded as being attained when the electrolyte content is small and remains substantially unaffected

⁸ Gouy, *Annales Physique*, 9, 7, 162, 1917.

⁹ Rideal, "Surface Chemistry."

by addition of electrolyte even up to and beyond the point at which the electrokinetic p.d. is reduced to zero.

Clearly the values attributed to q and ρ depend upon the values attributed to d_0 and K_0 respectively. It will be observed that we have to do with the ratio of these two quantities and on the basis of the numerical values employed K_0/d_0 has been set equal to 2.3×10^8 . As a check upon this value it may be pointed out that it would lead to a value of 20 microfarads for the electrostatic capacity, viz. $K_0/4\pi d_0$, for the "limiting" layer reckoned per unit interfacial area. This is almost identical with the capacity calculated by Stern,¹⁰ namely 24 microfarads from electrocapillary data at the *mercury-water* interface. Of course this does not imply that the charge density in the two cases is the same.

In the oil-water case when sufficient electrolyte has been added to cause the electrokinetic p.d. to decrease to zero—as shown by the absence of electro-phoretic movement—we infer that the actual p.d. at the interface, operating across the "limiting" rigid layer is given by $V_0 = 4\pi\rho d_0/K_0 = 0.71$ volt, on the basis of the value 4.3×10^4 for ρ .

The view set forth above regarding the gradual decrease in the thickness between the two "plates" of the double layer surface condenser with increase in electrolyte concentration is to be regarded as applying to the mobile portion of the layer alone. Simultaneously the "limiting" rigid layer with $d_0 = 3 \times 10^{-8}$ cm. exists in an incomplete form at electrolyte concentrations which are definitely below that required to cause the mobile layer to coalesce with the limiting rigid one. Thus for any concentration of electrolyte we can write in general:

$$q = q_1 + q_2,$$

where q is the (constant) charge on the core or oil surface, q_1 is the charge situated at the distance d_0 therefrom, and q_2 is the mobile charge situated farther out.

It is of interest to compare the value obtained for the total charge and charge density upon an oil droplet with that given by the usual Smoluchowski equations as applied to electrophoresis. Taking Tuorila's value namely 6.7×10^{-2} cm. per sec. under unit electrostatic potential gradient when minimal electrolyte is present it follows that the (maximum) value for ζ , the electrokinetic p.d., is 0.058 volt, this being based upon the value 5×10^{-7} cm. for the effective thickness of the mobile layer (the usually accepted value), the dielectric constant being at the same time set equal to 44, this being the mean of the normal value and the limiting minimum value. Corresponding to ζ the (maximum) value of q_2 , the electrokinetic charge, is 3×10^{-5} e.s.u., and the charge density 1.4×10^8 e.s.u.

If the above estimate for $q_{2\max.}$ is even moderately correct it leads to the important conclusion that even when conditions are most favourable the electrophoretic charge is only q_2/q namely $\frac{3 \times 10^{-5}}{8.5 \times 10^{-4}}$ or about 4 per cent. of the actual total charge on the oil droplet. In other words the distribution of ions in the composite double layer is such that nearly the whole of the charge on the core, viz. 96 per cent. or more is balanced by charges of opposite sign constituting a "limiting" rigid

¹⁰ Stern, *Z. Elektrochem.*, **30**, 508, 1924.

double layer ($d_0 = 3 \times 10^{-8}$ cm.) the remaining charges, constituting only 4 per cent. of the whole, being mobile.

In the light of the above conclusion it is perhaps scarcely remarkable that electrophoresis can be greatly diminished by very dilute solutions of electrolytes especially those of high valency.

The Case of the Air Bubble in Water.

Experimental investigations of air bubbles in water have been concerned to a large extent with the stability of foams, *i.e.* bubbles stabilised by soap, protein, or other chemical agents. In attempting to apply equation (3) or any of its derivatives to this case however, we ought to restrict ourselves to cases in which stabilisation is to be ascribed simply to the naturally occurring electric charge and surface tension.

With the object of seeing what kind of value is obtained for q by equation (4a) under conditions in which chemical stabilisers are absent, an approximate measurement of a was made in the writer's laboratory by measuring the rate of ascent of the air bubbles released by drawing off high pressure water from the town mains. The water when drawn off usually remains transparent for a few seconds, opalescence then appears which deepens into a milk-like emulsion. The average size of the air bubbles in this emulsion was obtained by applying Stokes' expression, in which the viscous force is equated to the gravitational pull, the distance traversed being suitably chosen to correspond approximately with a constant speed. It was thus found that $a = 5 \times 10^{-3}$ cm. Setting $\sigma = 73$ dynes/cm. and taking as before K_0 to have the value 7 and $d_0 = 3 \times 10^{-8}$ cm. it follows from equation (4a) that $q = 16.2$ e.s.u. and consequently the charge density $\rho = 5 \times 10^4$. This is even larger than the charge density at the oil-water interface, as is to be expected owing to the larger value of σ .

The above calculation is based on the assumption that the bubble size obtained is in fact an equilibrium value or, more accurately belongs to an equilibrium range of sizes. Evidence that this is the case is suggested by an observation of Alty.¹¹ Alty¹² had already shown that an air bubble when introduced into water takes some time before attaining a steady electric state. The purer the water the longer is the time. In the 1926 paper Alty remarks (p. 236), . . . "the experiments were repeated in water of specific conductivity 6×10^{-6} ohms⁻¹; in this water the charging up period is very short and the velocity of the bubble [in an electric field] increases steadily with decreasing radius [owing to the bubble dissolving in the water] until the latter is about 0.05-0.1 mm. At about this point the velocity is a maximum and thereafter decreases steadily until the bubble disappears. The explanation of the maximum is not clear. . . . At about this size (0.05 mm. diameter) the bubble ceases to be perfectly stable, and if accidentally disturbed it oscillates about the axis before returning to its equilibrium position." It would seem not improbable that the instability observed by Alty is due to a balance between the capillary effect and the electrical effect. The size of the bubble at which this occurs agrees well with that referred to above, which was obtained with tap water and consequently would be likely to reach an equilibrium state very rapidly in respect of electric charge.

¹¹ Alty, *Proc. Roy. Soc.*, **112A**, 235, 1926.

¹² *Ibid.*, **106A**, 315, 1924.

The air bubble in equilibrium is known to be negatively charged with respect to water. Taking the above value for ρ it follows that the p.d. across the "limiting" rigid double layer, namely V_0 , is 0.81 volt.

Further, in connection with the electrophoretic motion of the air bubble, Alty (1924) has found that $v_0 = 4 \times 10^{-4}$ cm. per sec. under 1 volt per cm. as the maximum velocity. Setting $d_{\max} = 5 \times 10^{-7}$ cm. as before, it follows that ρ_2 the electric density in respect of electrophoresis is 2.4×10^3 , a quantity which is 5 per cent. of the total charge density as calculated above. Further the (maximum) value of the electrokinetic p.d. is given by $\zeta_{\max} = 0.103$ volt on the basis that $K_{\text{mean}} = 44$. This is about twice as large as the electrokinetic p.d. at the oil-water interface.

An obvious criticism of the results obtained for ρ and V_0 is that they are unbelievably great. In fact the value for ρ , namely 5×10^4 , is just about one-fourth of the maximum possible charge density, viz. 1.96×10^5 calculated by R. S. Bradley¹³ on the basis that the p.d. is due to a complete unimolecular layer of dipoles oriented at right angles to the surface. On general grounds it is unlikely that a p.d. of this order would actually obtain at an air-liquid interface, especially in view of Alty's finding that in pure water appreciable time must be allowed to elapse to attain the final equilibrium charge density, thus pointing to diffusion of ions into the surface layer. It would thus seem much more probable that the total charge density is so low that there is almost no orientation in the surface layer which is entirely of the mobile type and that ρ approximates to ρ_2 namely, 2.4×10^3 . The absence of appreciable orientation at the interface would also imply that the dielectric capacity throughout the layer did not differ appreciably from that of water in bulk. Consequently $\zeta_{\max} = 0.056$ volt would represent in this case the total p.d. at the air-water interface. The condition of affairs at the air-water interface appears to be widely different from that at the water-oil interface.

Summary.

1. The total electric charge density on an oil droplet in an emulsion is calculated on the basis of a balance between the inwardly directed capillary pressure and the outwardly directed electrostatic pressure. On the basis of the existence of an electrical double layer of constant dielectric capacity expressions are obtained essentially the same as those derived by Knapp. The charge density is shown to be independent of the size of the droplet and a polydisperse system is therefore possible as an equilibrated system.

2. Comparison of the total charge as obtained above with the mobile charge responsible for electrophoresis shows that the latter is only a very small fraction of the total charge even under the most favourable conditions for electrophoretic movement.

3. In view of the mechanism postulated in the above treatment for the attainment of charge namely, by the adsorption of ions from the continuous medium, it is concluded that the treatment does not apply to those cases, e.g. colloidal electrolytes, in which the charge has its origin in surface ionisation of the colloidal material itself.

4. An examination of the air bubble case indicates that the surface conditions are very different from those at an oil/water interface, the electrokinetic or electrophoretic charge apparently accounting for the total charge in the case of the suspended air bubble.

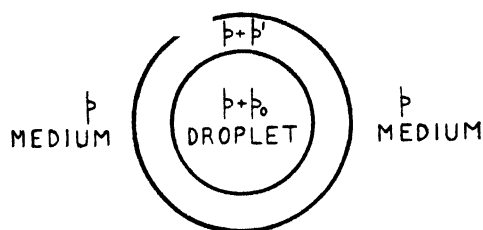
¹³ Bradley, R. S., *Phil. Mag.*, [VII], 11, 449, 1931.

APPENDIX.

ON THE PRESSURE INSIDE A LIQUID DROPLET SUSPENDED IN A LIQUID OR GASEOUS MEDIUM.

In the foregoing Paper the problem of the attainment of equilibrium size as a result of opposing electrical and capillary forces has been dealt with in terms of energy relations. For the present purpose we shall treat the same system from the point of view of force relations.

As before we regard an oil droplet, radius a , in an emulsion as being surrounded by an electrical double layer. The dielectric capacity is regarded as constant namely, K_0 , corresponding therefore to the condition of a very thin double layer of thickness d_0 . The uniform pressure



within the bulk of the homogeneous aqueous medium may be denoted by p , the pressure inside the oil droplet by $p + p_0$, (where p_0 is the excess pressure inside). p_0 may be positive or negative. Within the annular space between the two sides of the double

layer there is a pressure greater than p . The excess pressure within this layer is denoted by p' . It is necessary to postulate this positive excess in order to keep the two sides of the double layer apart. The charge on the oil droplet itself is $-q$, the charge on the outer sheath of the double layer being $+q$. The system is represented diagrammatically in the above diagram.

The force due directly to the electric charge $-q$ upon the inner sphere itself is an outwardly directed one amounting to

$$\frac{1}{2} \cdot \frac{-q}{K_0 a^2} \cdot \frac{-q}{4\pi a^2} \quad \text{or} \quad \frac{1}{8\pi K_0} \cdot \frac{q^2}{a^4}$$

per unit area.

The electrical forces acting upon the outer sphere or sheath are firstly an outwardly directed force due to the outer sphere acting upon itself and secondly an inwardly directed force due to the inner sphere acting upon the outer. These together amount to

$$\frac{1}{2} \cdot \frac{q}{K_0 (a+d)^2} \cdot \frac{q}{4\pi (a+d)^2} + \frac{-q}{K_0 (a+d)^2} \cdot \frac{q}{4\pi (a+d)^2}$$

i.e. an inwardly directed force amounting to

$$\frac{1}{8\pi K_0} \cdot \frac{q^2}{(a+d)^4} \quad \text{per unit area.}$$

In addition to the purely electrical forces we have likewise to take into account an inwardly directed force due to interfacial tension operative upon the inner sphere or oil "core" only. If the tension is σ , this inwardly directed force is $2\sigma/a$ per unit area. Further, within the annular layer we have an inwardly directed force of p' per unit area exerted upon the inner sphere and an outwardly directed force of the same magnitude

exerted upon the outer sphere. The equilibrium of the inner sphere is thus determined by the relation

$$p_0 + \frac{1}{8\pi K_0} \cdot \frac{q^2}{a^4} = \frac{2\sigma}{a} + p',$$

the equilibrium relation for the outer sphere being

$$\frac{1}{8\pi K_0} \cdot \frac{q^2}{(a+d)^4} = p'.$$

Eliminating p' we obtain

$$p_0 + \frac{q^2}{8\pi K_0} \left[\frac{1}{a^4} - \frac{1}{(a+d)^4} \right] = \frac{2\sigma}{a} \quad (a)$$

Since however d is small compared with a , equation (a) reduces to

$$p_0 + \frac{q^2}{2\pi K_0} \cdot \frac{d}{a^5} = \frac{2\sigma}{a} \quad (b)$$

Comparing this with equation (4) of the text deduced on the basis of energy considerations, *viz.*,

$$\frac{q^2}{4\pi K_0} \cdot \frac{d}{a^5} = \frac{2\sigma}{a},$$

it follows that the *excess* pressure p_0 inside the oil droplet at equilibrium is given by

$$p_0 = \frac{-q^2 d}{4\pi K_0 a^5} = \frac{-2\sigma}{a} \quad (c)$$

It follows from equation (c) that, even when the droplet has attained an equilibrium size, the excess pressure within it is *negative* and not zero as might perhaps have been expected on general grounds. Inserting the value for σ already employed in the text for an oil drop of radius 4×10^{-5} cm. it follows that $p_0 = -2.5 \times 10^6$ c.g.s. units = -2.5 atmospheres. Obviously if σ does not vary appreciably with curvature the negative excess pressure in a droplet varies inversely as the radius.

These negative values for the internal excess pressure indicate that the oil droplet is in a state of distension, which is diminished the larger the droplet. The act of coalescence with another droplet so as to leave the charge density unchanged would therefore be favoured in that the coalescence would decrease the degree of distension and the oil would approximate more towards its normal state. This effect should therefore be added to the decrease in surface energy which is usually regarded as one of the main factors in rendering an inelastic collision permanently effective so far as coalescence is concerned.

Turning for a moment to the magnitude of p' the excess (positive) pressure within the annular space constituting the electrical double layer, it is found by substitution of the numerical values already obtained that for an oil droplet of radius 4×10^{-5} cm. $p' = 2 \times 10^9$ c.g.s. units or approximately 2000 atmospheres. This from the definition of p' must be identical with the electric forces operative across a layer of the type considered.

In view of the above results, it is instructive to compare the system which we have had under consideration (namely, an electrically charged

oil droplet surrounded by an electrical double layer) with the case of a charged droplet in a non-conducting medium such as a gas, in which no double layer is supposed to be present, the charge being "free." In this case the outwardly directed force due to the electric charge is $2\pi\rho^2/K_0$, where $\rho = q/4\pi a^2$, is the charge density and K_0 the dielectric capacity in the immediate neighbourhood of the surface, *i.e.* a value presumably not far from unity. The excess pressure within the droplet is again represented by p_0 . The inwardly directed force is $2\sigma/a$.

Setting $K_0 = 1$ we thus have

$$p_0 + 2\pi\rho^2 = \frac{2\sigma}{a} \quad . \quad . \quad . \quad . \quad (d)$$

Taking the case of a charged growing water droplet in a non-conducting gas ($K = 1$) containing water vapour, and treating it from the point of view of energy relations we can write the total "free" electric + capillary energy in the form :

$$E = \frac{1}{2} \frac{q^2}{a} + 4\pi a^2 \sigma.$$

As before, we regard q as a constant.

Hence
$$\frac{dE}{da} = -\frac{1}{2} \frac{q^2}{a^2} + 8\pi a \sigma.$$

Hence the criterion, $\frac{dE}{da} = 0$, gives the relation :

$$\frac{1}{8\pi} \cdot \frac{q^2}{a^4} = \frac{2\sigma}{a} \quad . \quad . \quad . \quad . \quad (e)$$

for the critical size.

Comparing equations (d) and (e) it follows that when the critical size is attained $p_0 = 0$. This result was obtained many years ago by Sir J. J. Thomson (*cf.* "Applications of Dynamics to Physics and Chemistry"). Thus when the equilibrium size has been attained there is a sharp distinction to be drawn as regards the value to be ascribed to p_0 according as to whether a double layer exists or not.

Equation (e) applies to any value of the "free" charge q which the droplet may have picked up in the early stage of its growth. On applying the equation to the conditions in C. T. R. Wilson's experiments in which a single electronic charge acts as a nucleus for each of the droplets it follows that a single critical size would be expected. Setting $q = 4.8 \times 10^{-10}$ e.s.u. and $\sigma = 73$ dynes per cm. it follows from equation (e) that $a = 3.4 \times 10^{-8}$ cm. a quantity already obtained by Sir J. J. Thomson. As this quantity is of molecular dimensions it follows that it is necessarily incorrect, the error being due to the assumption that σ remains constant even when the curvature is exceedingly great. It is not improbable that under such extreme conditions σ would fall appreciably. Let us suppose that σ falls to 10 per cent. of its normal value. The resulting value for the equilibrium radius would then be 8.6×10^{-8} cm. Even this is almost certainly too small.

If we suppose that σ falls to 1 per cent. of its value at a plane surface we obtain 1.8×10^{-7} cm. which is a more plausible value. If it were possible to obtain by means of the ultramicroscope an average value for the true equilibrium size of the droplet (in the absence of supersatura-

tion) equation (e) would afford a means of obtaining the value of the surface tension at great curvature.

It has just been pointed out that in the case of a water droplet (suspended in air containing water vapour) and carrying a single "free" electron charge the equilibrium size is much smaller than that in the cloud actually observed. In the latter case if the charge is only that of a single electron the excess pressure as given by equation (d) must be *positive* and must approximate to $2\sigma/a$. If we take the visibility of the cloud as indicating that a is as large as 10^{-5} cm.¹⁴ it follows that p_0 is of the order of 15 atmospheres. If $a = 3 \times 10^{-4}$ cm. $p_0 = 0.5$ atmospheres. Obviously p_0 goes through a maximum, given by $a^3 = q^2/4\pi\sigma$. In the actual cloud experiments of course additional condensation takes place (owing to the supersaturation conditions) upon the walls of the vessel and upon the invisibly small droplets of equilibrium size, the extent of the subsequent growth of the droplets being arbitrary and dependent upon the amount of supersaturated vapour relative to the number of droplets in the vessel.

In experiments of the C. T. R. Wilson type in which the charge is comparable with that of a single electron it would seem that treatment of this charge as "free" is correct. On the other hand in experiments of the Millikan type in which charged oil (or other) droplets are produced by splashing or "atomisation" the charge is very large compared with that of the electron and the creation of a double layer cannot be excluded.

¹⁴ C. T. R. Wilson, *Phil. Trans.*, **189**, 265, 1897, mentions on p. 301: "When all diffraction colours disappear and the fog appears white from all points of view as it does when v_2/v_1 amounts to about 1.44, we cannot be far wrong in assuming that the diameter of the drops does not exceed one wave-length in the brightest part of the spectrum, that is, about 5×10^{-5} cm." Further, from the rate of fall of the cloud produced (when ionisation has been produced by Röntgen rays) Sir J. J. Thomson, *Phil. Mag.*, [V.], **46**, 528, 1898) has found the radius to be 3.4×10^{-4} cm.

*The University,
Liverpool.*

THE DETERMINATION OF THE MOBILITIES OF ANIONS OF WEAK ACIDS.

By CECIL W. DAVIES.

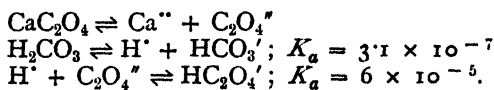
Received 26th May, 1932.

In determinations of the conductivities of salts it has been usual to subtract from the specific conductivity of the salt solution the conductivity of the solvent water, and this has been done even when one or other ion of the salt studied has acid or basic properties. Consideration shows that this cannot be correct, and Wynne-Jones¹ has already pointed out, without giving calculations, that this "normal" solvent correction is not applicable to salts of weak acids. Nevertheless, all the data in the literature seem to be affected by the same inaccuracy, which has led even in recent mobility determinations to errors of 5 per cent. or more, and it therefore

¹ Wynne-Jones, *J. Physical Chem.*, **31**, 1647, 1927.

seems worth while recording in detail an example taken from calculations made in preparing the following paper.

Scholder and his co-workers² in a series of valuable articles have reported the conductivities at very high dilutions of a number of metal oxalates. For a saturated solution of calcium oxalate monohydrate at 18° Scholder gives an equivalent conductivity of 101.3, this value being obtained by making the "normal" solvent correction. The second dissociation constant of oxalic acid is³ 6×10^{-5} , while the first dissociation constant is high enough to be left out of account, so that in the "equilibrium water" used by Scholder we have to deal with the equilibria:



The ionisation of the water itself, as we shall see, can be neglected, and the same is true in this instance of the second stage dissociation of carbonic acid. The first dissociation constant of the carbonic acid is taken from Kendall,⁴ who also gives 1.67×10^{-6} g-moles per litre as the total concentration of carbon dioxide in equilibrium water at 18°; we must assume that the conductivity of the water used by Scholder was practically entirely due to carbon dioxide.

The quickest way of finding the individual concentrations in the mixture appears to be by successive approximations. A curve is first constructed connecting the concentration of hydrocarbonate ion with that of hydrogen ion, by means of the relation⁵

$$[\text{H}^+] \cdot [\text{HCO}_3'] / (1.67 \cdot 10^{-6} - [\text{HCO}_3']) = 3.1 \times 10^{-7}.$$

A value is now assumed for $[\text{H}^+]$, and the corresponding value of $[\text{HCO}_3']$ is read from the curve, while the appropriate value of $[\text{HOX}']$ is obtained from the relation $[\text{HOX}'] = [\text{H}] \cdot (m - [\text{HOX}']) / 6 \times 10^{-5}$, m being the molar concentration of the salt. The correct values must satisfy the relationship: $[\text{H}^+] + [\text{HOX}'] = [\text{HCO}_3']$.

By analytical methods Scholder found the concentration of saturated calcium oxalate to be 0.000047. Using this value, the concentrations of the ions are found to be: $[\text{H}^+] = 15.7 \times 10^{-7}$, $[\text{HCO}_3'] = 27.6 \times 10^{-7}$, and $[\text{HOX}'] = 12.0 \times 10^{-7}$ g-moles per litre; it will be evident that the concentration of hydroxyl ion is about 5×10^{-9} , and therefore negligible. In equilibrium water itself the concentrations are:

$$[\text{H}^+] = [\text{HCO}_3'] = 21.3 \times 10^{-7};$$

since the hydrogen ion has about eight times the mobility of the hydrocarbonate ion, the conductivity of the carbonic acid is very much smaller in the presence of the calcium oxalate.

What we require for purposes of extrapolation or comparison is the "ideal" conductivity of the salt after allowance has been made both for the presence of the solvent ions and for their interaction with the salt. In the present instance we must deduct from the specific conductivity of the solution the conductivity of the hydrogen, hydrocarbonate and hydroxalate ions, and add to it an amount corresponding to the conductivity of the

² *Berichte*, 60, 1489, 1510, 1927; 63, 2831, 1930.

³ Cf. Gane and Ingold, *J. Chem. Soc.*, 2153, 1931.

⁴ *J. Amer. Chem. Soc.*, 38, 2460, 1916.

⁵ For the purpose of this paper the symbol $[\]$ is used indiscriminately for molar concentration and activity, although the author prefers, where ambiguity is likely, to use $\{ \}$ to indicate activity and $()$ to denote molar concentration. (*Note by Editor.*—It is hoped authors will adopt this convention.)

oxalate ions that have disappeared; mobilities at infinite dilution can be used as being sufficiently accurate for purposes of this correction. From the general equation: $\kappa = 10^{-3} \cdot \Sigma(z.m. \Lambda)$, where κ is the specific conductivity of a solution, and z , m , and Λ represent the valency, molar concentration and mobility of an ion, it follows that the solvent correction for the calcium oxalate solution is: $\Delta\kappa = -10^{-10}(15.7 \times 316.5 + 27.6 \times 40.1 + 12.0 \times 40 - 2 \times 12.0 \times 61.5) = -0.51 \times 10^{-6}$.

Making this correction in place of the full correction applied by Scholder increases the corrected conductivity by 0.3×10^{-6} , and gives 104.6 as the equivalent conductivity in place of Scholder's value 101.3. Since most series of conductivity measurements reach dilutions of the order considered in this example, *i.e.*, approx. 0.0001 *N*, whilst many organic acids are far weaker than that considered here, it is essential that the proper correction be applied to any measurements on salts of weak acids in water of relatively high conductivity.

Summary.

The solvent correction to be applied to conductivity measurements on salts of weak acids is described. In the example discussed the use of the "normal" correction leads to errors of many units in the conductivities, and hence in the mobility value derived from them.

*Battersea Polytechnic,
London, S.W. 11.*

THE EXTENT OF DISSOCIATION OF SALTS IN WATER. PART IV.: BI-BIVALENT SALTS.

By R. W. MONEY AND CECIL W. DAVIES.

Received 26th May, 1932.

In previous papers^{1, 2, 3} of this series the behaviour of uni-univalent and uni-bivalent salts in water up to concentrations of about 0.5 *N* has been examined. For each class a standard of behaviour was established by the fact that the conductivities of many salts in each group obey an extended form of Onsager's equation; departures from this standard of behaviour (which were always in the direction of an abnormally large decrease in conductivity with increasing concentration) were attributed to incomplete dissociation, and the dissociation constants calculated on this basis were found to explain other anomalous properties of the salt solutions concerned.^{2, 3, 4, 5} In the present paper the dissociation constants of some further bi-bivalent salts are reported.

For a bi-bivalent electrolyte in water at 18° Onsager's equation is: $\Lambda_x = \Lambda_0 - (142.8 + 1.272 \Lambda_0) \sqrt{C_i}$, where Λ_0 is the equivalent conductivity of the salt at infinite dilution, and Λ_x is the sum of the mobilities of the ions at an ion-concentration C_i (g-equivs. per litre). For an incompletely

¹ Davies, *Trans. Faraday Soc.*, **23**, 351, 1927.

² Righellato and Davies, *ibid.*, **26**, 592, 1930.

³ Banks, Righellato and Davies, *ibid.*, **27**, 621, 1931.

⁴ Blayden and Davies, *J. Chem. Soc.*, 949, 1930.

⁵ Davies, *ibid.*, 2410, 2421, 1930.

dissociated salt the equivalent conductivity is smaller than Λ_0 , and the degree of dissociation, α , is given by $\alpha = \Lambda/\Lambda_x$. If Λ_0 is known from the mobilities of the ions concerned, Λ_x and hence α may be found by a short series of approximations, or by the method of Banks,⁶ and the dissociation constant of the salt is given by: $K = \frac{f_{\pm}^2 \cdot \alpha^2 \cdot m}{(1 - \alpha)}$, where m is the molar concentration and f_{\pm} is the mean activity coefficient of the ions; the latter is calculated from the Debye Hückel equation: $-\log f_{\pm} = 2.80 \sqrt{C_i}$. At 25° Onsager's equation is: $\Lambda_x = \Lambda_0 - (1.284\Lambda_0 + 169.1) \sqrt{C_i}$, and the Debye-Hückel equation becomes: $-\log f_{\pm} = 2.84 \sqrt{C_i}$.

Calcium Sulphate.—Two series of measurements^{7,8} are available for calcium sulphate at 18° and are shown, with the results of the calculations, in Table I. The limiting equivalent conductivity of the salt was taken⁹ as 119.3.

TABLE I.

	$C \times 10^4$	Λ	α	K
Harkins and Paine .	1.0013	116.28	0.999	—
	1.9986	113.43	0.9346	0.0053
	4.9871	109.00	0.9662	0.0052
	9.9755	103.82	0.9415	0.0051
McGregory . .	1	114.9	0.9873	0.0034
	2	113.8	0.9881	0.0068
	5	109.3	0.9681	0.0055
	10	104.3	0.9450	0.0055

The values of K are satisfactorily constant; the mean value is 0.0053.

Cobalt and Nickel Sulphates.—Measurements have been made by Franke¹⁰ at 25°. Mobilities at this temperature are not accurately known; that of the sulphate ion has been taken as 79, whilst values for Co (55.5) and Ni (56.2) have been estimated from Franke's conductivity measurements on the chlorides.

TABLE II.

	$C \times 10^4$	Λ	α	K
Cobalt . . .	9.768	115.1	0.9149	0.0033
	19.53	107.2	0.8750	0.0035
			Mean:	0.0034
Nickel Sulphate . . .	9.768	117.4	0.9281	0.0040
	19.53	109.3	0.8880	0.0040
			Mean:	0.0040

Calcium Oxalate.—Scholder¹¹ has determined the concentration and the conductivity of a saturated solution of the monohydrate at 18°. The concentration is 0.094×10^{-3} g-equivs. per litre, and the conductivity,

⁶ Banks, *J. Chem. Soc.*, 3341, 1931.

⁷ MacGregory; *Landolt-Bornstein Tabellen*, 746, 1905.

⁸ Harkins and Paine, *J. Amer. Chem. Soc.*, 41, 1155, 1919.

⁹ Davies, *Conductivity of Solutions*, p. 181, 1930.

¹⁰ Franke, *Z. physikal. Chem.*, 16, 463 1895.

¹¹ Scholder, *Berichte*, 60, 1510, 1927.

after applying the hydrolysis correction described in the preceding paper, is 104.6. Taking ⁹ Λ_0 as 112.8, these figures give: $\alpha = 0.9500$, $K' = 0.00075$. Scholder's two determinations do not show very good agreement, however, and probably the true values may be as high as: $\Lambda = 106.7$, $\alpha = 0.9692$, $K' = 0.00127$. That the uncertainty is so great is due to the high dilution and the magnitude of the solvent correction; the value $K' = 0.001$ will be adopted.

Strontium Oxalate.—Scholder gives the figures; $C = 0.672 \times 10^{-3}$ g-equivs. per litre, $\Lambda = 99.1$; applying the hydrolysis correction makes the latter figure 99.9. Taking ² $\Lambda_0 = 115.0$ gives $\alpha = 0.927$, $K' = 0.0029$.

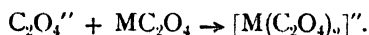
Barium Oxalate.—A series of measurements on this salt has been made by Scholder, beginning with the saturated solution, to which known amounts of water were added. The results are given in Table III., Λ_0 being taken ⁹ as 116.6.

TABLE III.

$C \times 10^3$	1.72	4.12	5.15	5.88	6.86	7.72	10.29
Λ	114.8	108.3	106.7	105.8	104.6	103.4	100.7
α	>1	0.978	0.970	0.964	0.959	0.951	0.936
K'	—	0.0067	0.0060	0.0056	0.0055	0.0051	0.0047

There is a pronounced drift in the figures, but this is not surprising in view of the great difficulties of the work; in the most dilute solution the solvent's conductivity amounts to 12 per cent. of the whole, and the smallest contamination in the transferences of liquid would lead to high values for Λ and K' . The value for the saturated solution is probably, therefore, the most reliable.

Oxalates of the Transitional Metals.—Dilution curves have also been obtained by Scholder and his co-workers^{11, 12} for the sparingly soluble oxalates of Mn^{++} , Fe^{++} , Co^{++} , Ni , Zn and Cd . For all these the measured conductivity is abnormally small, and this is attributed by the authors to complex anion formation according to the equation



In most cases, however, we find that the conductivity figures give no evidence of this. For an extremely stable complex anion, an example of which has been reported by Sidgwick and Lewis,¹³ the ionisation reaction is $2MA \rightleftharpoons M^{++} + MA_2^{--}$, and since the number of molecules is unchanged by dilution the conductivity will also be approximately constant; the apparent dissociation constant, calculated in the ordinary way, will therefore increase in proportion to the concentration. Such an extreme case is not likely to be found at high dilutions, but it will be evident that if increase in the concentration of a salt is accompanied by marked amounts of complex ion formation, this will evidence itself in a rising value of the dissociation constant. This is not found for the Zn , Cd , Mn , and Co -salts. Table IV. shows the data for cadmium oxalate ($\Lambda_0 = 107.4$) and is typical of the results obtained.

Some of the results for the more soluble manganese oxalate ($\Lambda_0 = 107.0$) are given in Table V.

¹² Scholder and Linström, *Berichte*, **63**, 2831, 1930.

¹³ Sidgwick and Lewis, *J. Chem. Soc.*, **129**, 2538, 1926.

TABLE IV.

$C \times 10^4$	0.31	1.24	1.99	2.84	3.31	3.72	4.97
Δ	106.3	83.8	73.8	66.5	63.5	61.4	55.2
α	>1	0.801	0.710	0.642	0.614	0.594	0.537
$K \times 10^4$	—	1.76	1.48	1.37	1.35	1.34	1.25

TABLE V.

$C \times 10^4$	0.497	1.950	4.690	8.840	18.78	42.92	75.10
Δ	97.9	74.7	57.9	46.6	35.7	25.5	20.3
α	0.932	0.721	0.5653	0.4590	0.3571	0.2611	0.2119
$K \times 10^4$	2.88	1.54	1.39	1.33	1.34	1.28	1.27

Here only a few of our calculations are reproduced; actually, Scholder and Linstrom measured the conductivity of nineteen solutions in the concentration range 0.0002 – 0.0075*N*, and for all these measurements the irregular variation in K lies between the limits $1.39 - 1.26 \times 10^{-4}$.

With both these salts, as also with zinc oxalate and cobalt oxalate, the values of K are satisfactorily constant, when allowance is made for the difficulties of the work. Indeed, the figures for manganese oxalate, extending as they do from high dilutions down to a degree of dissociation of only 20 per cent., provide a particularly good example of a typical weak salt the simple ionisation of which conforms to the law of mass action. The figures for these salts therefore leave little room for doubt that the abnormally low conductivities of the saturated solution are due primarily to the presence of electrically neutral molecules. At the same time, it must be agreed that the oxalates do evince a tendency to form complex ions in the presence of soluble oxalates; this is shown by Scholder's other work, and is being investigated by us by means of solubility measurements. It may well be, therefore, that auto-complex formation does occur to a small degree in the saturated solutions we have considered but that its influence on the conductivities is obscured by a compensation of errors. Even though this be so, the constants we have derived for the primary process of dissociation will not be greatly in error, and can be accepted for the purpose of making a general survey of the extent of dissociation in bi-bivalent salts.

For the two remaining salts, the conductivities do provide evidence of auto-complex formation. For ferrous oxalate the "dissociation constants" increase steadily from 2×10^{-6} in the most dilute solution ($C = 3 \times 10^{-5}$) to 5×10^{-5} in the saturated solution ($C = 49 \times 10^{-5}$); the true increase, after allowing for unavoidable contamination of the solutions, is probably greater. This shows that the ferro-oxalate ion is very stable, as of course is known from other evidence, and indicates that the primary dissociation constant of ferrous oxalate is less than 2×10^{-5} . Nickel oxalate also shows an increasing dissociation constant over the limited concentration range available for study, and the true dissociation constant must be less than 5×10^{-6} .

Discussion of Results.

The results of these and earlier calculations are collected in Table VI., to which some results of Riley and Fisher¹⁴ and Ives and Riley¹⁵ for the

¹⁴ Riley and Fisher, *Y. Chem. Soc.*, 129, 2006, 1929.

¹⁵ Ives and Riley, *ibid.*, 1998, 1931.

malonates at 25° have been added. Riley and co-workers employed Ostwald dilution formula constants in their studies of these salts; for better comparison we have recalculated the data to the same basis as the other figures.

TABLE VI.— $K \times 10^4$ FOR BI-DIVALENT SALTS.

	Sulphate.	Oxalate.	Malonate.
Mg	63	3.7	16
Ca	53	10	—
Sr	—	29	—
Ba	—	47	—
Mn	—	1.3	—
Fe	—	<0.2	—
Co	34	0.20	—
Ni	40	<0.05	0.73
Cu	45	—	0.025
Zn	45	0.13	2.1
Cd	38	1.3	5.1

Attention may be called to two points brought out by this table. One is the great differences that exist among the dissociation constants. Cowperthwaite and La Mer¹⁶ have shown that the Gronwall, La Mer and Sandved extension of the Debye-Hückel equation will explain the behaviour of zinc and cadmium sulphate solutions on the basis of ionic radii derived from crystal structure measurements; it will be obvious that this treatment could not be successfully applied to other salts, e.g., copper malonate.

The other noteworthy feature of table VI. is the series of values for the oxalates of the alkaline earth metals, and it is interesting to compare these values with those of other salts of the alkali and alkaline earth metals. The nitrates, sulphates and some other salts of the alkali metals show the more ionic association in water the greater is the atomic number of the metal.^{1, 2} The same is true of the alkali metal salts so far investigated in methyl and ethyl alcohols; Hartley¹⁷ has correlated this apparent regularity with the corresponding increase in the mobility of the cation, and suggests that ionic association in these hydroxylic solvents is greatest for cations of small (solvated) diameter. Turning to the salts of the Group IIA metals, for which the ionic mobility again increases with atomic number, a similar position seemed to be revealed by the earlier figures; the dissociation constant of the nitrate is smallest for barium and greatest for magnesium, and the same is very possibly true of the sulphates.

The behaviour of the oxalates is in striking contrast with these regularities, since the dissociation constants increase uniformly from magnesium to barium. Although quantitative data are only available in this instance, it is unlikely that the oxalates are unique; they seem to be resembled by the hydroxides in water, and by the thiocyanates in methyl alcohol¹⁸; unfortunately there are no data for these salts in water. The comparisons show, therefore, that even for a restricted group of typical salts such as those of the alkali and alkaline earth metals in water, ionic association cannot be explained in terms of ionic radii alone, whether hydrated or non-hydrated radii are used. On the other hand it must be agreed that a fuller

¹⁶ Cowperthwaite and La Mer, *J. Amer. Chem. Soc.*, **53**, 4333, 1931.

¹⁷ Sir H. Hartley, *Chemistry at the Centenary Meeting of the British Association*, p. 25, 1931.

¹⁸ Unmack, Murray-Rust and Hartley, *Proc. Roy. Soc.*, **127A**, 228, 1930.

explanation in terms of the relative co-ordinating tendencies of anion and solvent molecule for a given cation demands more knowledge than we possess at present of the various factors involved.

Summary.

The dissociation constants of some bi-bivalent salts in water have been calculated from conductivity measurements, and are found to vary between wide limits. For some salts of the Group IIA metals the dissociation constants decrease regularly from magnesium to barium, whilst for others the reverse order is found to hold.

*Battersea Polytechnic,
London, S. W. 11.*

REVIEWS OF BOOKS.

Practical Steelmaking. By WALTER LISTER. (London : Chapman & Hall Ltd. Price, 25s. net.)

The manufacture of steel in the open hearth or electric furnace really constitutes an exceedingly interesting—and exceedingly complex—problem in physical chemistry. The problem comprises, *inter alia*, the solubilities of various gases, metallic oxides and silicates in the molten steel and the equilibrium conditions between more or less oxidised metal and various types of slags, the latter being possibly acid, basic or neutral in character but always complex mixtures of oxide.

The problem is also one presenting very considerable difficulties to the would-be investigator; among these, apart from the complexity, may be mentioned the high temperature at which the process takes place, the lack of a suitable refractory container which is unacted on by metal or slag and, finally, the fact that at present it is probably not possible to estimate accurately the total oxygen content of steel or to determine exactly the forms in which this oxygen exists in the solid metal.

It is not to be inferred that the problem has not been tackled; a very considerable amount of research has been done by metallurgists as regards the influence of slag conditions, temperature, rate of oxidation and other factors on the quality of the steel produced. In spite of all this investigation, however, steelmaking is still largely an art and for that reason very difficult to describe in written language. Steelmelters with years of experience behind them can note subtle differences in the appearance of the molten slag and metal in the furnace or in the way in which the refining of the metal progresses, and can turn these differences into account in producing good steel; but it is not easy for them to describe these appearances to any one who is not himself familiar with them; for one thing, there are no accepted terms by which the steelmaker may describe what he observes.

Mr. Lister's book is an attempt—and a very praiseworthy one—to give an account of what happens in the making of good steel. And in so far as these happenings can be described in ordinary English terms, the author succeeds very well. Thus he tells us, with a considerable amount of detail, how to start up a steelmelting furnace, how to run it efficiently and how to repair it when necessary; in short how to make it an economical unit for the production of steel. But when he comes to describe the actual melting and refining of the steel, he is less happy and considerably less expansive in his descriptions; largely, as suggested above, because there are no words which adequately convey to a reader the precise meaning of these details in the art of steelmaking.

Mr. Lister's book is intended mainly for steel metallurgists. It has, however, this point of interest to physical chemists, that it makes evident the difficulties of preparing commercially and in a reasonably deoxidised and slag-free condition, large quantities of a metal which is easily oxidised and which, either in its metallic or more or less oxidised forms, attacks to a greater or less extent the refractory materials in which it has to be handled while molten.

J. H. G. M.

The Metallic State: Electrical Properties and Theories. By W. HUME-ROTHERY, M.A., PH.D. (Oxford, Clarendon Press (Humphrey Milford), London, Oxford University Press, 1931. Roy. 8vo. Pp. xx + 372, with 66 figures. 25s. net.)

In this valuable book Mr. Hume-Rothery deals in a thorough and comprehensive manner with the electrical and thermal properties which characterise the metallic state. Although the metallurgist, even the "Practical Metallurgist," may not wholly deserve the strictures of the preface, there is no doubt that metallurgy will gain much from an increasing recognition that, as a branch of science, it consists essentially in the application of physics and chemistry to the study of metals and alloys. Thus metallurgical fact and theory must be brought into the closest relation with the general body of physical and chemical fact and theory. The ultimate dependence on atomic structure of those aspects of the behaviour of metals and alloys in which the metallurgist is usually interested, and the necessity of considering the properties of metals in relation to their positions in the Periodic Table will be realised by students of this book, which has been written as a step towards a connected theory of physical metallurgy. That we still have very far to go, if the author's estimate of the present state of knowledge is correct, is indicated by his concluding sentences (p. 342): "The unsatisfactory position of the electronic theories of metals is largely the result of attempts having been made to erect detailed and complex mathematical theories, in order to explain facts for which accurate and systematic knowledge is almost entirely lacking. The need at the present time is not so much for further mathematical developments, but rather for a thorough and systematic determination of the electrical constants of metals, with special reference to their connexion with the Periodic Table and atomic structures. . . . For the present we may say that the problems in connexion with the electrical properties of metals remain essentially unsolved. But they are unsolved through lack of systematic and reliable experimental knowledge—not of theoretical speculation." It is only fair to add that in the reviewer's opinion this discouraging pronouncement does much less than justice to the large amount of systematic and accurate data collected in this book, and to the progress, so clearly indicated by Mr. Hume-Rothery, made towards its theoretical explanation.

The first half of the book consists of a critical review of published work on electrical and thermal properties, successive chapters dealing with the electrical conductivity of pure metals, of primary metallic solid solutions, of secondary solid solutions and intermetallic compounds, the thermal conductivity of pure metals and of alloys, the thermo-electric properties of metals and alloys, emission phenomena, and contact electricity of metals. Much of the information is collected from sources which lie outside the usual reading of metallurgists.

The second half of the book is theoretical and gives clear and readable accounts, in historical order, of the various electronic theories of metals, from the simple free electron-gas theory of Drude to the electron lattice theory of Lindemann and the Sommerfeld theory, based on quantum mechanics, with its later modifications by Houston, Bloch, and others. Non-mathematical explanations of the theories are given wherever possible. A concluding chapter, of

remarkable interest, starts with a brief account of the periodic classification of the elements and its interpretation in terms of atomic structure. The crystal structures of the metals and their dependence on atomic structure, interatomic distances in the crystals, the nature of the metallic type of bond, the composition and nature of solid solutions and intermetallic compounds in relation to atomic structure, the problems of conductivity and supra-conductivity are then discussed in a most illuminating manner.

The printing and binding are of the high standard maintained by the Clarendon Press. In the diagram on page 43 it is obvious that "104° C." should be "– 104° C."

The book can be warmly recommended to all metallurgists and to physicists and chemists interested in the subject. Mr. Hume-Rothery has performed a most useful service in collecting into one volume so much related but hitherto widely scattered knowledge.

H. M.

"The Interference of Electrons." Edited by P. DEBYE. Translated from the German by WINIFRED M. DEANS. (London: Blackie & Son, Ltd., 1931. Pp. vi + 85. Price 7s. 6d.).

In 1930 a conference was held in Leipzig on the interference of electrons, at which papers were given by Rupp, Wierl, Mark and Mott on the diffraction and interference of electrons, and by Gruneisen, Bloch and Peierls on the electronic conduction of metals. These papers were subsequently published in book form in German and their importance justifies their translation into English.

Rupp reviews the experimental results of the diffraction of slow electrons at crystal surfaces and shows what deductions can be made as to the internal potential of crystals. Chemists will be particularly interested in Wierl's paper on the scattering of electrons by molecules in the vapour state. There are some beautiful reproductions of diffraction patterns of carbon tetrachloride, 1-1-dichloro-ethane, and 1-2-dichloro-ethane. He discusses the evidence as to the distances between carbon atoms in aromatic and aliphatic bonds and refers to the new evidence now available as to the mobility of molecular groups about the single and double bonds of carbon. Mark and Mott give the theories of the scattering of electrons and X-rays and consider the results open to experimental verification.

Gruneisen gives a valuable comparison of the results of recent theories of metallic conduction with the results of experiment. He proposes a semi-empirical formula for the variation of electrical conductivity of temperature which represents the facts over a very wide range. The theoretical difficulties of calculating the mutual interaction of the conduction electrons in metals—one of the most difficult outstanding problems of the metallic state—is ably discussed by Bloch and further theoretical difficulties of the electron theory of metals are reviewed by Peierls.

These short reviews of important problems are extremely stimulating. They are certain to suggest new points of view and new problems to all who read them and by their publication a valuable contribution is made to scientific knowledge.

ERRATUM.

P. 520. The equation on line 13 should read

$$\frac{dx}{dt} = kK \cdot \frac{K_3}{[Cl^-]_m \{K_3 + [Cl^-]_m\}} \cdot \frac{[HC_2O_4^-]}{[H^+]_m} \cdot (a - x).$$

* SOLUBILITY AND ACTIVATED ADSORPTION.

BY E. W. R. STEACIE.

(Received 30th May, 1932.)

In a previous paper¹ I showed that the slow processes accompanying adsorption could be explained completely on the basis of the known solubility of gases in metals, and that, while activated adsorption might exist, the evidence cited by Taylor² in its support was entirely inconclusive.

In the course of the discussion at the recent Faraday Society Symposium on the adsorption of gases by solids, Taylor states³ that my contention was quite unjustified since "the quantities of gas involved are one or two orders greater than the well-determined solubility data of the gas in question." In support of this statement he gives a table comparing solubility and adsorption data for hydrogen and nickel, hydrogen and copper, and oxygen and silver. This table is extremely misleading as is shown below.

(a) Oxygen and Silver.

Taylor compares the adsorption of 30.7 c.c. per 100 grams found by Benton and Elgin at 110° C.⁴ with the solubility of 1.49 c.c. per 100 grams found by Johnson and the writer at 200° C.⁵ In their paper Benton and Elgin state that four-fifths of the gas was taken up rapidly, and the remaining one-fifth slowly. Hence the gas which is claimed to represent activated adsorption is only one-fifth of the amount given, *viz.*, about 6 c.c. The solubility of oxygen in silver increases rapidly with decreasing temperature, and while the form of the isobar at low temperatures is not known, the solubility must be at least 3 c.c. per 100 grams at 110° C., and may easily amount to the entire 6 c.c. In any case the solubility and the supposed activated adsorption are certainly not of different orders of magnitude.

Furthermore, in the solubility experiments referred to above the silver used was in the form of thick sheets, and the solubilities may therefore be considered to represent gas which is uniformly distributed throughout the lattice. In the oxygen-silver system, therefore, at least the major portion of the slow sorption and possibly all of it, can be explained on the basis of true solubility, without the necessity of assuming concentration at the grain boundaries.⁶

* A contribution to the General Discussion on the Adsorption of Gases.

¹ Steacie, *J. Physical Chem.*, **35**, 2112, 1931.

² Taylor, *J. Am. Chem. Soc.*, **53**, 578, 1931.

³ Taylor, *Trans. Far. Soc.*, **28**, 444, 1932.

⁴ Benton and Elgin, *J. Am. Chem. Soc.*, **48**, 3027, 1926.

⁵ Steacie and Johnson, *Proc. Roy. Soc.*, **112A**, 542, 1926.

⁶ Ward, *Proc. Roy. Soc.*, **133A**, 506, 1931.

(b) Hydrogen and Copper.

Here again Taylor compares the total adsorption, not the slow portion, with the solubility. The older values of the solubility obtained by Sieverts are used, rather than those obtained by Ward in his recent thorough investigation of the system. This system need not be referred to further since Ward has already replied to Taylor's criticisms.⁷

(c) Hydrogen and Nickel.

As before the *total* adsorption is compared with the solubility. The solubility data of Sieverts are used.⁸ Sieverts' results are unquestionably inaccurate at low temperatures. Thus in one typical description of his experimental procedure he states that a gas and metal were heated from 20° to 800° and cooled to 300° in 158 minutes, pressure readings being taken en route. It is apparent that equilibrium would never be established at low temperatures under such conditions.

It is probable that the solubility would increase at low temperatures in this system as with silver and oxygen, and there is some theoretical support for such a view.^{9, 10}

It may therefore be concluded that, whether activated adsorption actually exists or not, the quantities of gas taken up in slow processes accompanying adsorption measurements are at least of the same order of magnitude as the amounts dissolved. There is, therefore, no unequivocal proof of the existence of activated adsorption. If such activated adsorption does exist, all calculations of activation energies, etc., have been made on composite adsorption—solubility effects, and are probably several hundred per cent. in error.

*Physical Chemistry Laboratory,
McGill University,
Montreal, Canada.*

THE SWELLING OF WOOL FIBRES IN WATER AND IN AQUEOUS SOLUTIONS OF SODIUM HYDROXIDE, AS SHOWN BY THE CHANGE IN CROSS-SECTIONAL AREA.

BY MABEL H. NORRIS, M.Sc.

(*Wool Industries Research Association.*)

Received 5 May, 1932.

The phenomenon of swelling of wool fibres in water and solutions of alkali has long been known. Much of the available data is, however, of a qualitative character, and there appears to be little information as to the manner of this swelling, with the exception of certain measure-

⁷ Ward, *Trans. Far. Soc.*, **28**, 445, 1932.

⁸ Sieverts, *Z. physik. Chem.*, **77**, 611, 1911.

⁹ Steacie and Johnson, *Proc. Roy. Soc.*, **117A**, 662, 1928.

¹⁰ Simons, *J. Physical Chem.*, **36**, 652, 1932.

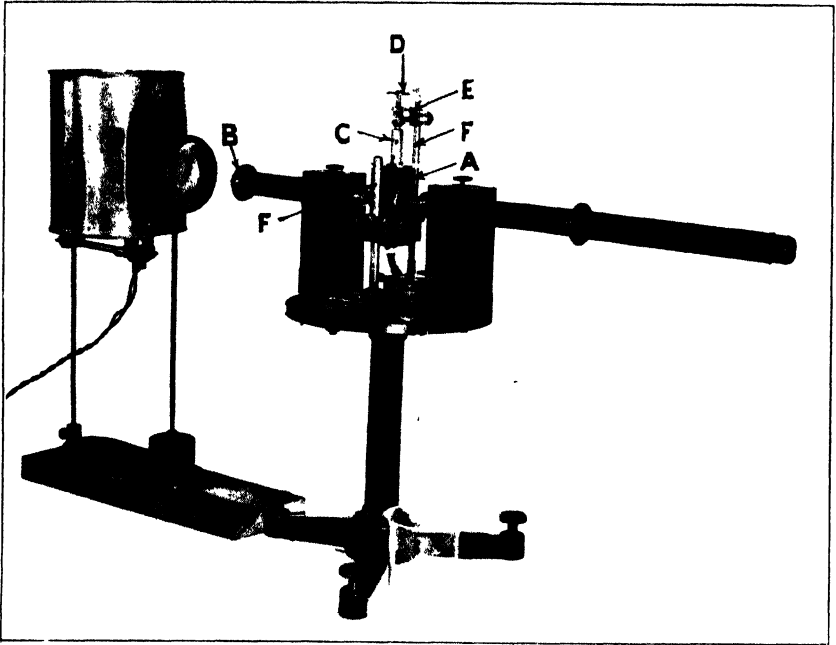


FIG. 1

(To face page 619.)

ments by Hirst¹ all optical measurements having been made by the observation of one diameter of the fibre only.

The present paper is an account of the first part of an investigation undertaken with the object of determining accurately the amount and manner of swelling of wool fibres in water and in different solutions and liquids, in order to throw more light on the changes which the wool fibre must undergo during the process of milling.

Hirst used a modified form of Polikeit apparatus to measure the change in area of cross-section of the fibre, rather than merely one diameter. The chief disadvantage of his form of apparatus was the small amount of liquid which his immersion cell would contain. Evaporation caused great inconvenience when dealing with volatile solvents, and made accurate concentrations of aqueous solutions difficult to maintain if the experiment was continued for any length of time.

Hirst studied the change in cross-sectional area along the whole length of the fibre during swelling, by taking a series of readings (as the fibre was rotated) at successive definite points, and then calculating the value of the mean major and mean minor axis. Such average results, did not, of necessity, furnish detailed results of exactly what was happening at any particular point. In the present work attention has been concentrated on a definite point of the fibre, as it seemed that such measurements would yield interesting information with the necessary accuracy.

Apparatus.

A square ebonite cell (A) (see Fig. 1) was designed, into the opposite walls of which were screwed pieces containing microscope slide cover slips, forming windows. One of these served for observation, the other for illumination purposes. The observation window projected inwards into the cell. The source of illumination was a 100 watt lamp, the light from which passed through a 3-inch glass condenser and then down the condenser tube of the optical system, which was similar to that employed with an Einthoven Galvanometer. This tube was closed at the end by means of two glass discs (B); one blue, the other of ground glass. The insertion of these glasses improved the definition of the image considerably. The edges of the fibre were clearly defined, and it was possible to read the diameter of the fibre to the nearest 0.5 of a small division of the micrometer scale.

The fibre holder consisted of a rotating head (C) from which the fibre hung. It was made of a thin steel rod, connected with a horizontal disc (D) graduated in degrees, which was fixed into the top of a hollow outer cylinder about $\frac{3}{4}$ in. in diameter. Three adjusting screws in the outer cylinder made it possible to centralise the fibre after it was in place. The fibre was cemented to the end of the steel rod with dental cement and the joint covered with Goodall Acid Seal paint No. 1011. This paint was found to resist alkali fairly well, and as the joint was not under the solution, served to protect it adequately from any contact with alkali during the filling of the cell.

The lower end of the fibre was secured to a four-vented platinum sinker by threading it through a small central hole and then closing the hole with a platinum plug. The sinker was small and light, in order to minimise the tension on the fibre, but it was adequate to prevent any twisting

¹ W.I.R.A. pubns., Nos. 17, 31; 1922, 1924.

as the fibre was turned about its axis, and insufficient to cause any stretching of a normal, fairly coarse fibre, even when it was kept in the solution for weeks at a time.

The ebonite cell, although quite watertight, was found to leak slightly at the joint round the window when sodium hydroxide solutions were used. Further, the ebonite tended to sorb the sodium hydroxide. In order to overcome these difficulties the cell was heated to 65°C . and dipped (before the windows were screwed in) into high melting-point paraffin wax (m.p. 60°C .). The screw pieces, also hot and previously dipped in the paraffin wax, were then screwed in and the cell wiped on the outside and allowed to cool. This procedure resulted in a very thin but complete coating of paraffin wax on the inside of the cell, so that no part of the ebonite was exposed to the action of the caustic soda, and there was no leaking at the joints. The top was closed by means of a split ground glass plate which fitted closely round the rotating head which carried the fibre. This was smeared with vaseline as was also the under surface of the plate.

By means of the inwardly projecting observation window it was possible to get the objective of the microscope near to the fibre. In order to increase the magnification, and at the same time not to reduce the working distance, the length of the tube of the microscope was doubled. The final length of the tube was 15.25 ins., and this modification was found to give the desired result.

Each fibre, before examination, was marked at intervals along its length with small touches of acid seal paint. A fine adjustment (E) at the top of the fibre holder enabled the fibre to be moved up or down slightly in a vertical direction until a suitable spot for examination (near one of these paint marks) was found. Such a mark ensured measuring the fibre at exactly the same place every time. In most cases the change in length of the fibre was remarkably small, although the increase in cross-sectional area was sometimes as much as 80 per cent.

The cell, and the rotating head from which the fibre hung, were held in position entirely independently of each other, by means of clamps from uprights fixed to the circular brass plate which also held the solid metal blocks through which the microscope and condenser tubes passed. Each of these uprights (F, F') was movable in a horizontal direction, so that it was possible to move the cell and the fibre, independently of each other, until they were in the required positions; that is, the fibre in the centre of the field of vision, as close to the glass as possible, but swinging just free of it.

It was found that by means of the adjusting screws in the rotating head of the fibre holder, it was possible to centralise the fibre very accurately, so that on rotation it hardly moved out of focus.

Experimental Method.

The wool fibres used were taken from a sample of Greasy Lincoln Wethers. Previous to use they were washed in several changes of warm benzene, air dried and stored in a corked test-tube.

Each fibre examined was fixed to the rotating head of the apparatus, as described above, centralised and then left untouched until the end of the series of observations which sometimes lasted many weeks.

The fibre was first measured in glycerine^a then in water and then in solutions of sodium hydroxide. The fibres were left in the solution for at least an hour and often longer before the final readings were taken.

The cell was filled through the top by means of a pipette, after removing half of the ground glass cover. It was drained through the stop-cock at the bottom. Before any observation the cell was well rinsed (by filling and emptying three times) with the solution about to be used.

The micrometer eyepiece was standardised against the micrometer standard scale in the usual way with the following results:—

26.00 small divisions of the eyepiece scale equal 6 small divisions of the standard = 0.06 mm. That is, one small division of the eyepiece scale = 0.002308 mm. However, the readings were not converted to absolute units but recorded as direct readings from the micrometer eyepiece scale.

Measurements of the width of the fibre were made at intervals of 12° through a rotation of 180°. The largest and smallest widths found were recorded as the *a* and *b* axes of the fibre. The product of *ab* was taken as representing the cross-sectional area of the fibre and *a/b* the circularity ratio.

Preliminary Experiments.³

In most of these experiments a series of solutions of sodium hydroxide, increasing in concentration by about 0.025*N* from 0.01*N* to 0.125*N*, were used. Concentrations greater than 0.125*N* caused considerable breakdown in some fibres. In a few experiments, after the concentration 0.125*N* was reached, a further series of measurements was made in solutions of decreasing concentration down to 0.01*N* sodium hydroxide, then water, then glycerine. This cycle was repeated.

As the preliminary experiments were carried out before the apparatus was in its final form, the data obtained were rather inaccurate and are not recorded. However the general results obtained were valuable in that they indicated those likely to result from more accurate experiments. All the conclusions suggested by the preliminary investigation, which were tested by accurate experiments in the later work, were substantiated. The data from these later experiments are now presented.

Experimental Data.

Firstly, in order to discover the normal behaviour of a fibre, and thus form a basis of comparison for later work, five fibres of the Greasy Lincoln Wethers wool were each carefully measured, (1) in glycerine, (2) in water, (3) in 0.05*N* NaOH, (4) in water, (5) in glycerine, (6) in water, (7) in 0.05*N* NaOH, (8) in water, and (9) in glycerine. In each case readings were taken at intervals, until two or more consecutive readings gave the same result. The data are recorded in Table I.

^aGlycerine dehydrates the fibre so that its size is the same as it would be in dry air (Hirst).

³The fibres used in these experiments were cleaned by washing in warm alcohol and ether instead of benzene, and had been stored in glycerine.

TABLE I.—PERCENTAGE SWELLING * OF FIVE FIBRES OF LINCOLN WETHERS WOOL IN WATER AND IN 0.05N NaOH SOLUTION.

	1.	2.	3.	4.	5.	Mean Swelling. Per Cent.
Water .	32	33	32	36	34	33
0.05N NaOH	74	54	58	87	60	67
Water .	46	48	48	55	48	49
Glycerine .	0	0	0	0	0	0
Water .	44	48	48	55	48	49
0.05N NaOH	74	57	58	87	60	67
Water .	52	48	48	55	48	50
Glycerine .	0	0	0	0	0	0

* Increase from size in glycerine.

The data presented in Table I. show that the percentage swelling of different fibres in water is constant within the experimental error.⁴ The mean value obtained (33 per cent.) is in good agreement with Speakman and with Hirst, both of whom record 32 per cent. increase in the cross-sectional area of a Cotswold wool fibre at 100 per cent. relative humidity.

The percentage swelling in 0.05N NaOH, however, is not constant (even assuming the largest possible experimental error), but varies from fibre to fibre.

The size of the fibre in the second sample of water, although larger than in the first, again appears to be constant within the experimental error, and to be independent of the amount of swelling which has taken place in the 0.05N NaOH. The third water value, after treatment with glycerine, is always the same as the second.

The size of the fibre in the second sample of 0.05N NaOH was the same as in the first, and the fourth water value, after the second treatment with NaOH, was the same as the second and third, while the size of each fibre in glycerine was always the same both before and after treatment with water and 0.05N NaOH solution.

The time of soaking necessary to ensure maximum swelling was difficult to determine accurately as the filling and rinsing of the cell took up some time. However, an approximate estimation of the minimum time necessary was made, although these times were greatly exceeded, the fibre being left in contact with the same solution in most cases for about 12 hours. The initial swelling in 0.05N NaOH and the subsequent shrinking in water following this solution were the slowest processes, taking at least 2 hours. In all other cases 10 or 15 minutes appeared adequate. The reaction in glycerine is very quick indeed, and the final value was usually obtained in the first reading after filling.

Cycle of NaOH Solution.—Careful measurements were next made of the behaviour of three fibres when subjected to the series of NaOH solutions used in the preliminary experiments, the cycle being repeated once. The results are recorded in Fig. 2.

⁴ The percentage experimental error varies with the size of the fibre being measured. The readings were taken correct to the nearest 0.5 of a micrometer division. It has been calculated that for these Lincoln fibres the *maximum* experimental error in the percentage increase in area of the fibre is about 10 per cent.

Each of the three fibres measured gave exactly the same type of curve, which is illustrated in Fig. 2, where the mean swelling of the three fibres in each concentration of alkali is given. The fibres show a steady increase in size up to $0.05N$ NaOH, followed by a more gradual rise to $0.125N$. Treatment from this point with solutions of alkali in decreasing concentration shows a very interesting result, namely, the fibres do not change in size, however long they are left in contact with more dilute solutions, until a concentration of $0.025N$ or below is reached. Even then the decrease in size is only slight and the value obtained in water is about 20 per cent. greater than with water in the first instance, even after prolonged soaking in water.⁵

Repetition of the cycle gave the curve which is indicated by the broken line. It will be seen that, within the experimental error, water and each of the NaOH solutions causes the fibre to return to the size it

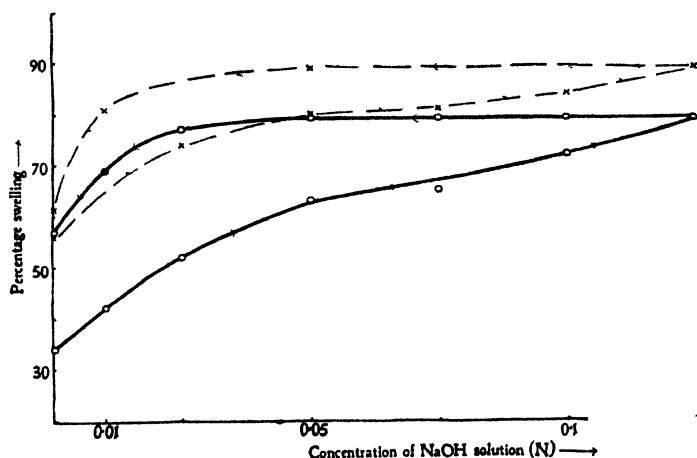


FIG. 2.—Percentage swelling of Lincoln Wether wool fibres in increasing and decreasing concentration of NaOH solutions (mean of 3 fibres).

was during the descending part of the first curve, except in the most concentrated solution ($0.125N$) where there is a distinct tendency for this value to be exceeded. Decreasing concentrations had just the same effect as before. The fibre was measured in glycerine between the two cycles and at the end of the second cycle and was found to be the same size as at the beginning of the experiment; that is, no permanent swelling or shrinking of the dry fibre was effected by the treatment given, although the size of the wet fibre was permanently altered, for a fibre thus treated swells 20 per cent. to 30 per cent. more in water than before treatment.

Such behaviour may be considered in the light of recent X-ray investigations.⁶ A wool fibre photographed in water shows an X-ray photograph identical with that of a dry fibre. In other words, the water goes into the fibre between the micelles and leaves the X-ray photograph unaltered. With NaOH solution, however, the photograph is altered

⁵ In one experiment after six weeks soaking, in water that was changed four times during the period, a decrease of only 3 per cent. in the size of the fibre was obtained.

⁶ Astbury: *privately communicated*.

because the solution *penetrates* the micelles, pushing apart the protein chains and altering the structure of the fibre. Thus *after* treatment with NaOH water can penetrate into the fibre not only between the micelles but *within* them and a fibre thus damaged, on further treatment with water, swells more than it did before contact with alkali because the available surface for sorption of water has been increased in extent according to the amount of damage caused to the fibre by the alkali. The dehydrating agent, glycerine, removes the water molecules and the fibre returns to its original size.

The fact that the fibre does not at first decrease in size with decreasing concentration of NaOH points to the conclusion that the point of equilibrium of the chemical reaction between the NaOH and the wool is well over to one side, the side of the product of the reaction, and that therefore until the concentration of NaOH is very much reduced the equilibrium is not noticeably disturbed. However, when the concentration of NaOH reaches nil and the fibre is allowed to soak in water its increased size is unlikely to be due to the retention of alkali because in glycerine the fibre immediately returns to its original size, and further, when again placed in water, quickly reattains the size it possessed in water at the end of the cycle of NaOH solutions.

Stretched Fibres.—Having so far examined what appeared to be normal fibres we next investigated the behaviour of fibres that had been stretched 30 per cent. of their length and permanently set by steaming. The results are collected in Table II.

TABLE II.—PERCENTAGE SWELLING IN WATER AND 0.05N NaOH SOLUTIONS OF FIBRES OF LINCOLN WETHERS WOOL WHICH HAD PREVIOUSLY BEEN STRETCHED 30 PER CENT. OF THEIR LENGTH AND PERMANENTLY SET BY STEAMING.

	1.	2.	3.	4.	Mean Swelling. Per Cent.
Water	36	45	42	41	41
0.05N NaOH	86	38	87	87	87
Water	62	61	64	55	60.5
Glycerine	0	0	Fibre broke	0	0
Water	62	61	—	55	59
0.05N NaOH	86	38	—	87	87
Water	62	61	—	55	59
Glycerine	0	0	—	0	0

Comparison of the results shown in Table II. with those recorded in Table I. shows at once that the stretched fibres swell appreciably more than do unstretched fibres. This was to be expected because recent X-ray work by Astbury has shown that the extended protein chain (β -keratin) is more vulnerable than the normal folded chain of α -keratin. It is not surprising, therefore, that NaOH solutions can more easily thrust apart the protein chains within the micelles. The supposition stated above that such damage increases the available surface for subsequent sorption of water gains support by these results in that after treatment with alkali the swelling in water is 60 per cent. as contrasted with only 41 per cent. before contact with alkali.

On immersion in water, all of these fibres stretched slightly; on the first immersion in NaOH they stretched considerably (a rough estimation

gave the amount of this stretching as about 7 per cent. of the length of the fibre). This may have been partly due to the tension of the platinum sinker on the weaker fibre. However, a rough experiment to find if the fibres stretched in alkali when under no tension indicated an increase in length of 3 per cent. or 4 per cent.

Fibres which had been treated with Pauli Reagent.—It was thought that the reason for the inconsistency of the percentage swelling in 0.05*N* NaOH (see Table I.) might have been partly due to the fact that inadvertently some of the fibres used were perfect whilst others were slightly damaged.⁷ A small bunch of fibres was therefore treated with Pauli reagent and four fibres selected which were not stained at all by the reagent. These were measured in exactly the same way as the fibres of Table I. The results are collected in Table III.

TABLE III.—PERCENTAGE SWELLING OF FOUR FIBRES OF LINCOLN WETHERS WOOL WHICH WERE HARDLY STAINED BY IMMERSION IN PAULI REAGENT.

	1.	2.	3.	4.	Mean Swelling. Per Cent.
Water .	31.5	31	40	25	32
0.05 <i>N</i> NaOH .	54	76	66	56	63
Water .	47	46	54	45	48
Glycerine .	0	—3	0	0	—1
Water .	47	46	54	45	48
0.05 <i>N</i> NaOH .	54	76	66	56	63
Water .	49	46	57	45	49
Glycerine .	11	3	5	0	3

It will be seen that the results obtained agreed very well with the data of Table I, the mean results differing by only 1 per cent. in the case of water and 4 per cent. in the case of the 0.05*N* NaOH solutions. However, the percentage swelling of the individual fibres in the alkali differed almost as much as in the measurements recorded in Table I., the smallest swelling being 54 per cent. and the greatest 76 per cent., a difference of 22 per cent., well outside the experimental error. It is not possible, therefore, to explain away this discrepancy as due entirely to damage, as all these fibres were known to be undamaged according to the Pauli test, and even supposing the chemical treatment they received during the test affected their swelling capacity, the error involved should have been constant. It appears most likely, therefore, that the different amount of swelling shown by different fibres in 0.05*N* NaOH, is due to some innate chemical difference in the fibres themselves. It must be remembered that water sorption appears to be a purely physical phenomenon (at any rate in the case of all fibres that are not severely damaged with NaOH), whereas with solutions of alkali chemical reaction also comes into play. Herein probably lies the true explanation of the differences, for the more that is known about the wool fibre the more it is realised that chemical and physical differences do exist, not only from fibre to fibre but even in different parts (root and tip) of the same fibre.

⁷ W. von Bergen (*Melliand*, 1930, 2, 9-15; 186-192) has drawn attention to the increased swelling of damaged fibres in NaOH solutions as compared with undamaged fibres.

That damage does indeed cause increased swelling is clearly demonstrated in Table IIIA. The fibre continued to swell in 0.05*N* NaOH until it finally became so tender that it broke.

TABLE IIIA.—PERCENTAGE SWELLING OF A FIBRE, WHICH WAS DARKLY STAINED BY IMMERSION IN PAULI REAGENT, IN WATER AND IN 0.05*N* NaOH.

	Water.	0.05 <i>N</i> NaOH after :—			
		$\frac{1}{2}$ Hr.	2 Hrs.	19 $\frac{1}{2}$ Hrs.	24 Hrs.
Per cent. swelling	39	84	107	200	215 fibre broke.

A single experiment with a fibre that had been subjected to prolonged exposure to ultra violet light also indicated an increased swelling in 0.05*N* NaOH but not in water. The percentage increase in cross-sectional area in water was 33 per cent. and in 0.05*N* NaOH 91 per cent. after half an hour, when the fibre broke.

p_H of NaOH Solutions.

The p_H of the solutions used were determined by measurement with a Cambridge Hydrogen-ion Apparatus (Outfit B) and the following results obtained. These figures are included to facilitate comparison between the effect of NaOH solutions on wool with that of other alkaline solutions to be used in later work.

Concn. of NaOH (<i>N</i>)	0.0093	0.050	0.0750	0.101	0.123
p_H	12.2	12.9	13.1	13.2	13.3

Circularity Ratio.

One of the objects of this investigation was to determine whether, on swelling, the wool fibre changed the shape of its cross-section. The collected data have been carefully studied, and it has been calculated that in order to be significant a change of 0.04 or more in the circularity ratio is necessary. It is quite evident that no such differences exist except in the initial stages, the mean difference between the circularity ratio in water and 0.05*N* NaOH, or between one NaOH solution and another, being usually 0.01 and never more than 0.03; that is, there is no change in shape of the wool fibre either as it swells or as it subsequently shrinks.

The author's thanks are due to Dr. S. G. Barker, Director of Research, for suggesting the problem and for the interest he has taken in the work; to Mr. N. Tunstall for assistance in the design of the apparatus; to Mr. Astbury for helpful discussion; and to Mr. J. Amos, foreman of the Association's workshops, for so efficiently constructing the apparatus. Finally, grateful acknowledgement is due to the Research Control Committee of the Wool Industries Research Association for permission to publish this paper.

THE ELECTRODEPOSITION OF CHROMIUM FROM TERVALENT CHROMIUM SALT SOLUTIONS. PART II. CHROMIUM ACETATE, OXALATE, AND TARTRATE BATHS.

BY HUBERT THOMAS STANLEY BRITTON AND OLIVER BRENTWOOD
WESTCOTT.

(Received 23rd May, 1932.)

It was shown in Part I.¹ that although metallic chromium could be deposited from solutions of chromium chloride and sulphate, the deposits are never free from basic matter and, in consequence, their general character is poor. The cause of this failure is intimately connected with the relatively low p_H at which insoluble basic matter is precipitated from solutions of simple chromium salts. The work described in this paper consists of attempts to use trivalent chromium salt solutions of such enhanced stability that electrolysis could be carried out at high p_H values without the risk of the deposits being contaminated by precipitated matter.

Britton² has shown that solutions of chrome alum to which varying amounts of either sodium acetate, oxalate or tartrate had been added, and then boiled or allowed to stand for some time, became resistant to precipitation when treated with alkali at ordinary temperatures. This suggested that it might be possible to prepare similar solutions of the concentrations necessary for electrolysis and which might be electrolysed without the separation of basic matter. Before proceeding with the electrolysis of these solutions the effect of variation of p_H was investigated electrometrically in the same manner as with the simple salts (*cf.* Part I.).

Acetate Solutions.

The preparation of these solutions at concentrations of chromium salts suitable for deposition purposes led to some difficulty, on account of the formation of insoluble gummy precipitates, which could not be re-dissolved even on boiling. It was finally found possible to prepare solutions which were 0.5 or 1.0 Molar with respect to chromium chloride and up to 3.0 Molar with respect to sodium acetate. Since the previous history of the solution is of importance with regard to its behaviour with increasing p_H , the method of preparation was standardised as far as possible: the initial difficulty resulted in the first solutions being prepared by boiling, and it was only after further work that solutions were prepared in the cold by long shaking. All the boiled solutions were violet by transmitted light and red by reflected light, while those containing more than 1.5 mols. of acetate to 0.5 mols. chromium salt were also violet when prepared in the cold. Those of lower acetate content retained the green colour of the chromium chloride.

¹ *Trans. Far. Soc.*, **27**, 809, 1931.

² *J. Chem. Soc.*, 269, 1926; see also Britton, *Hydrogen Ions*, second edition, 1932, 432.

(a) Electrometric Titrations.

The results of the effects of p_H change on these solutions are summarised in Fig. 1. which shows the p_H obtaining in the course of titration of 100 c.c. of the solution with 2.0 Molar caustic soda.

The compositions of the solutions corresponding to curves A, B, C, and D, were 0.5 Molar chromium chloride, and 0.5, 1.0, 2.0, and 3.0 Molar sodium acetate respectively. These were boiled for five minutes in preparation. Solutions E, G, and F were 0.5 Molar chromium chloride, and 0.5, 1.0, and 2.0 Molar sodium acetate respectively. These solutions were prepared in the cold. A solution corresponding to D in composition could not be prepared in the cold.

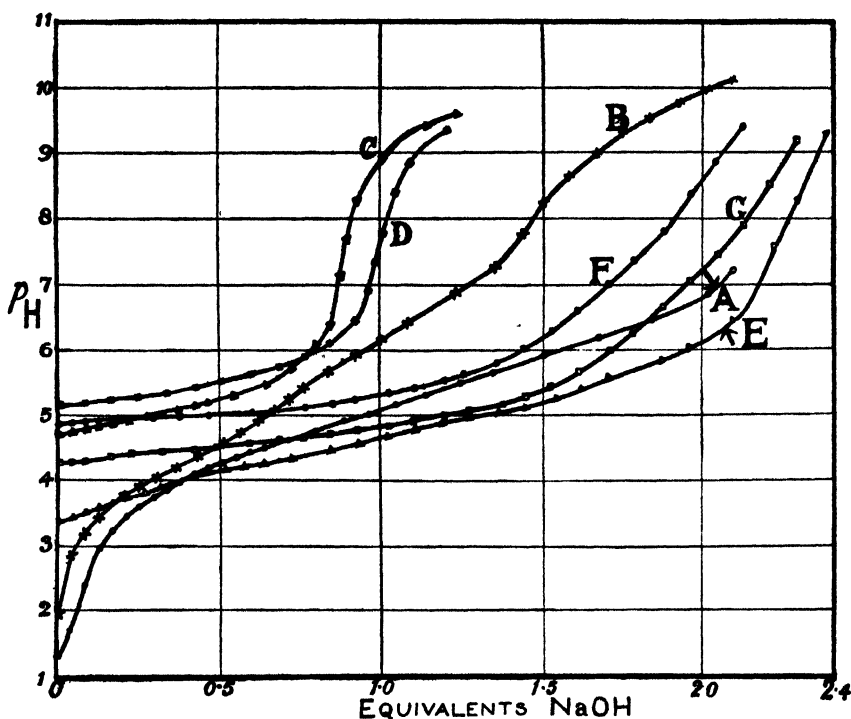


FIG. 1.

Except in the case of solutions containing the lowest amounts of acetate, none of the solutions yielded a precipitate, even when the p_H had attained a value much greater than the normal precipitation limit of 5.3, for solutions of the chloride and sulphate. The greater part of the curves lies between the p_H values 4-6, and there is ample evidence of a large buffer capacity in each case, followed by a more or less abrupt rise to very alkaline values. With the solution corresponding to curve B, it was found that, on standing over-night after the titration a firm gel-like mass was formed.

The other solutions, however, did not give precipitates on standing, after being rendered alkaline. Since the p_H of acetic acid is 4.74, the buffer range shown by a mixture of sodium acetate and acetic acid is 3.7-5.7, *i.e.*, from 10 per cent. to 90 per cent. neutralisation. This is

almost the same range as that shown by the solutions under discussion, a fact which indicates that free acetic acid is produced. This can only occur with the hydrolysis of the chromium acetate first formed from the interaction of chromium chloride and sodium acetate. The hydrolysis thus results in the formation of a basic acetate, and the functioning of these solutions as electrodeposition media will depend on the structure of this basic complex, the extent to which it ionised, and the nature of the ions produced. The requisite p_H conditions are thus obtained and the solutions, superficially, should yield good deposits.

(b) Electrolysis.

Despite the apparently satisfactory conditions prevailing in these solutions, it was impossible to obtain good deposits. The solutions electrolysed were of the following compositions: 0.5 and 1.0 Molar with respect to chromium chloride and 1.0, 2.0 and 3.0 Molar in sodium acetate. Solutions prepared both in the cold and after boiling, were electrolysed in cells, without and with a diaphragm, and, in the latter case, various salt solutions were used as anolytes as well as the chromium solution itself. The cathodes were of copper, with platinum anodes, as in Part I. Runs were also made at temperatures of 40° and 60° C. Except for one case, the deposits were uniformly poor, being basic matter of varying colour and thickness, from very thin iridescent films to heavy granular layers. However, a solution, 0.5 Molar with respect to chromium chloride and 3.0 Molar with respect to sodium acetate, heated just to boiling and cooled quickly, gave, on first electrolysis at 20-30 amp./dm.², a thin deposit of smooth, bright metal of good adherence; a second electrolysis of the same solution gave only basic matter, but a freshly prepared solution gave good metal, again only for the initial run. Although the results were generally bad, the last result suggests that a suitable type of solution had been found and it was thought that oxalate solutions might give better results. Similar investigations with the chromium as sulphate were not carried out.

Oxalate Solutions.

The concentration range possible for the oxalate solutions is more restricted than with the acetates; it is impossible to prepare them in the cold. When this was attempted, a fine light green precipitate was produced, which would not dissolve on shaking or standing, but did so on heating to boiling, the solution becoming violet-red. With early attempts to prepare concentrated oxalate solutions, the low solubility of the sodium salt led to difficulties, and ammonium oxalate, however, gave better results. The solutions finally used for electrolysis were of the following composition: 0.5 Molar chromium chloride, with 0.5, 1.0, and 1.5 Molar ammonium oxalate; 1.0 Molar chromium chloride, with 1.0 and 2.0 Molar ammonium oxalate. Similar solutions with the chromium added in the form of the green sulphate were also prepared.

(a) Electrometric Titrations.

The whole series of these is not given, but the curves marked A and B in Fig. 2 are typical and represent the titration of 100 c.c. of a solution 0.5 Molar in chromium chloride (A) or 0.25 Molar in chromium sulphate (B) with 1.0 Molar ammonium oxalate. Here again, precipitation

did not occur, but the curve is markedly different from those of the acetate solutions, in that the initial rise in p_H is much more abrupt and there is no buffer action.

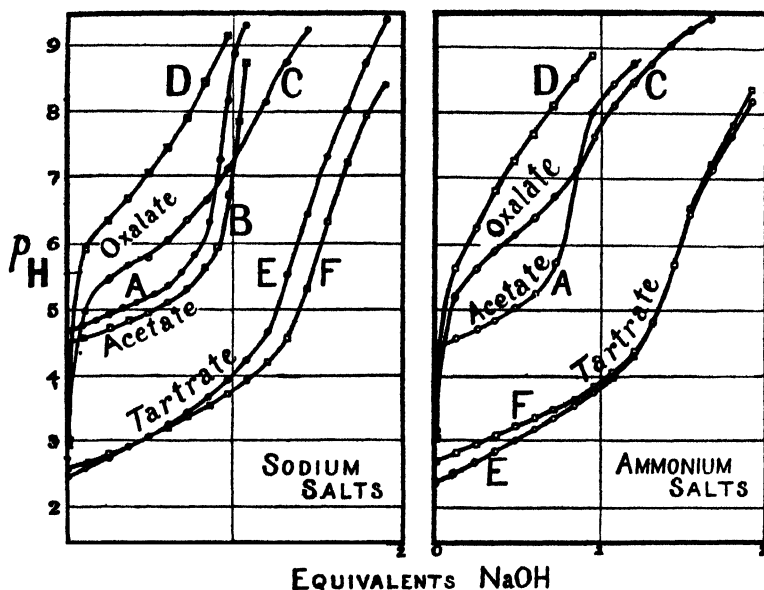


FIG. 2.

(b) Electrolysis.

The discrepancy between theoretical expectations and practical results found with acetate solutions, was repeated with these solutions, though not so markedly. Electrolysis under varied conditions of current density, temperature, etc., gave a little metal, but this was of excellent quality. The use of the green sulphate in place of the chloride made little difference. However, when solutions of composition 0.25 Molar in basic chromium sulphate (prepared by the reduction of chromic acid with sulphur dioxide) and 1.5 Molar in ammonium oxalate, which had been boiled thirty minutes, were electrolysed at 30-50 amp./dm.² in a diaphragm cell with or without foreign anolytes, and with platinum anodes, very good deposits of smooth bright adherent metal were obtained. The better results with oxalate solutions deflected interest from tartrate solutions and they were only cursorily examined. Similar methods of investigation showed that, although the deposits are better than those from acetate solutions, there was nothing to equal the excellent deposits from oxalate solutions. Attention was now directed to the further examination of the latter solutions.

Further Investigation of Oxalate Solutions.

The success of the basic-sulphate oxalate combination may be due to the maintenance of a suitable p_H or to the formation of a stable complex, or to both of these factors. The acetates, however, in solution, exhibited a favourable p_H range, but gave poor results; hence, it would appear that the complex formed in the case of the oxalates possesses greater stability in alkaline solution and does not so readily hydrolyse

to produce insoluble basic matter. In an endeavour to prepare solutions the initial p_H of which could be varied by the addition of alkali, the solubility of the sodium salt was re-examined and solutions 0.25 *M.* with respect to chromium sulphate and 1.5 *M.* sodium oxalate were prepared. These were electrolysed in a cell without a diaphragm at 20-50 amp./dm.² and during the course of electrolysis, the p_H changed from 4.0 to about 10. In each case, no metal was obtained but only brown or green basic matter. Repetition with a diaphragm cell gave similar results. These experiments suggest that the ammonium-ion exerts some specific effect. There are two possible explanations; that the ammonium-ion forms a cationic complex of the ammine type with the chromium-ions, and so maintains suitable conditions for good metal deposition; or that, at the high p_H values set up during electrolysis, the caustic soda set free from the sodium salt exerts a much stronger action on the oxalate complex than does ammonium hydroxide set free similarly from the ammonium salt, and hence, basic matter is much more easily produced in the former case. Several series of extended runs were made to determine the life of the solutions, and it was found that after a short initial period in which poor deposits were formed, good metal could be obtained after as much as 30 amp. hour electrolysis. The poor deposit from the first electrolysis was due to the low p_H , since, on standing, the alkaline value reached in electrolysis gradually fell to about p_H 3.4. An attempt was made to prepare a solution of twice the concentration, *viz.*, 0.5 *M.* chromium sulphate and 3.0 *M.* ammonium oxalate. This could not be done, but a solution at this concentration of chromium with 2.0 *M.* ammonium oxalate was made and showed a greater stability than the more dilute solution over long periods of electrolysis. The effect of current density on the cathode efficiency was next examined; it was already known that the efficiency was very low, of the order of 1.0 per cent. The gasometric method for the analysis of the deposits, described in Part I. could not be used here as the volume of gas evolved was generally less than 1.0 c.c. A method was adopted which, while it did not give the purity of the deposit, sufficed to show whether deposits of 100 per cent. purity were obtained. The weight of the deposit was determined before and after treatment with dilute hydrochloric acid. The chromium in the acid solution was estimated by oxidation with sodium peroxide in alkaline solution and iodimetric titration of the sexavalent chromium thus produced. If the deposit is metal only, then the chromium determined in the solution should be equal to the weight of the deposit, but, if any impurity such as oxide matter be present, the weight of chromium found volumetrically will be less than that of the deposit. Hence the method gives an indication of the purity of the deposit but does not determine the actual weight of metal present, and the current efficiency cannot accurately be found. On analysing the deposits obtained from the basic sulphate-oxalate solutions described above, the hydrogen given off contained considerable amounts of hydrogen sulphide. This could only come from sulphur compounds introduced by the sulphur dioxide used in preparing the sulphate. The latter solution was boiled to remove excess sulphur dioxide, but apparently a little remained after this treatment, and cathodic reduction converted it to hydrogen sulphide, part of which became occluded in the cathode deposits. Several deposits showed a dark blue tinge, and the odour of hydrogen sulphide was very strong in the gas from the acid treatment. When similar deposits were allowed to stand, the metallic lustre gradually

632 CHROMIUM ACETATE, OXALATE, AND TARTRATE BATHS

disappeared and gave place to dark powdery layer which fell away from the electrode. This suggests that slow interaction had occurred between metal and sulphur impurity. In order to avoid this source of impurity, another form of chromium sulphate was used, a violet powder corresponding to $\text{Cr}_2(\text{SO}_4)_3$ with 16.70 per cent. of chromium. A solution of the same composition as when using the basic sulphate was electrolysed with platinum anode and copper cathodes and gave very good deposits, of bright, smooth metallic appearance and good adherence. Typical results are given in the table below :—

No.	C.D. Amp./dm ² .	Time of Run in Minutes.	Weight of Deposit.	Purity.	Remarks.
1	0	60	0.0030	72.80	{ Thin brown film left after acid treat- ment.
2	30	60	0.0037	85.40	
3	40	60	0.0035	86.40	{ Clean dissolution.
4	40	60	0.0046	88.75	
5	50	60	0.0060	89.10	
6	50	240	0.0258	86.50	
7	50	240	0.0391	89.40	
8a	50	240	0.0370	87.10	{ Clean dissolution. Two portions of same deposit.
8b	—	—	0.0307	87.00	
With nickel cathodes.					
9	40	30	0.0035	76.60	{ Clean dissolution.
10	50	39	0.0068	70.40	
11	50	240	0.0197	78.70	

No hydrogen sulphide was noticed in the gas produced in dissolution but an odour suggestive of hydrocarbons was observed. This points to carbon as impurity, produced by cathodic reduction of the oxalate. Electrolyses for periods up to twenty-four hours at 50 amp./dm.² were carried out to obtain thicker deposits. Nickel and copper cathodes were used, and except for a tendency to crack and blister at the edges, the deposits were as good as the thin deposits.

The function of the ammonium ion in promoting good metal deposition is peculiar and a comparative study of the acetate, oxalate and tartrate solutions, using both the sodium and ammonium salts was made in order to throw more light on this subject. The results of further electrometric investigation are summarised in Fig. 2, which represents the titration of 100 c.c. of each solution with 2.0 *M.* caustic soda.

The composition of the solutions is as follows: 1.0 *M.* in chromium and A and B, 2.0 *M.* acetate, C and D, 2.0 *M.* oxalate, E and F, 2.0 *M.* tartrate. A, C and E were prepared with the chromium as chloride, B, D, and F, were prepared with the chromium as sulphate. On electrolysis under comparable conditions of current density, etc., the sodium salt solutions all gave poor results, chiefly basic matter with a little discoloured metal; the ammonium salts gave better results but except for the oxalate solution, which gave its customary good deposits, these were also comparatively poor. Hence, only the ammonium oxalate solutions will give satisfactory, and slightly better results are obtained by using the chromium as sulphate. A consideration of the

curves in Fig. 2 shows that while the acetate and tartrate curves are convex towards the alkali axis, the oxalate curves are concave. This means that the OH^- -ion added is not very rapidly removed in the latter case, and hence little decomposition of the complex occurs. It is possible that this greater stability is the reason for the difference in the results obtained from these solutions. The constitution of these solutions is not sufficiently well understood to allow of profitable consideration at this point and the matter is being studied further.

The foregoing observations are in general accord with those recently made by Mazzuchelli³ who secured good chromium deposits from ammonium chromioxalate solutions at an efficiency of 1.4 per cent. by employing C.D.'s of 25-150 amp./dm.². Increases in either acidity or temperature militated against chromium deposition.

Cathode Potential Current Relationships.

In view of the unsatisfactory state of the existing knowledge of the ionisation of chromium salt solutions and the ease with which metallic chromium is rendered passive, it appears highly improbable that the reversible potential corresponding to $\text{Cr}^{3+} \rightleftharpoons \text{Cr}$ can be determined with any measure of certainty. This is particularly true of the complex oxalate solutions from which the good deposits of chromium were obtained.

Where, however, more than one process can occur at an electrode, the curve representing the variation of cathode potential with current density shows more or less marked breaks corresponding to the onset of a new cathode reaction. The cathode potential-current density curve for the oxalate solution described above was determined, using the usual Luggin attachment for the normal calomel electrode, in conjunction with a potentiometer system. The cathode was of copper and the anode of platinum. Readings were taken when the potential was steady at a given current density, and the current then increased by means of a rheostat. The evolution of hydrogen led to the formation of bubbles in the capillary, and this was loosely plugged with cotton wool to prevent breaking the circuit. At the end of the determination, the cathode was covered with a thin layer of smooth, bright metal.

The cathode potential curve showed no sudden break, hence it is impossible to infer anything with regard to a second cathode reaction. The first reaction is the evolution of hydrogen, and the potentials shown throughout are those that would be set up by a hydrogen electrode, when due consideration is taken for the effect of overvoltage, and the variation of the p_{H} of the solution during electrolysis.

Similar experiments with the simple salts led to inconclusive results. It would appear that the reaction resulting in metal deposition is responsible for such a small part of the transference of the current that it is unable to set up a characteristic potential, so that it is completely masked by that causing hydrogen evolution.

General Conclusions.

The foregoing experiments reveal that it is extremely difficult, if not impossible, to deposit pure chromium from tervalent chromium salt solutions. Even in those cases in which excellent metal appeared to have been deposited, analysis showed that some contamination, which,

³ *Atti. Acad. Lincei*, 12, 587, 1930.

however, was not visible, had occurred, and in view of the fact that insoluble basic matter often remained behind on the cathodes after the chromium had been dissolved away in hydrochloric acid, it appears that the impurities must have been deposited in the initial stages of the electrolyses. The experiments have, however, confirmed the view that the most successful baths were those of high p_H and containing the chromium in as stable a complex as possible. Regarding the particular oxalate baths that gave the greatest promise, the results obtained suggest that the ammonium-ion had a beneficial effect on the course of electrolysis, probably due to less destructive action of ammonium hydroxide, produced during electrolysis, on the chromium-bearing complex.

The current efficiency of chromium deposition is exceedingly low whether the cathodes be copper or nickel. Increase of concentration, of current density, and the use of a diaphragm, all tended to give higher efficiency of deposition whilst increases in temperature generally led to the formation of poorer deposits. Regarding the use of organic salts, oxalates were distinctly better than either acetates or tartrates.

Grateful acknowledgement is made of the assistance given to one of the authors (O. B. W.) by the Exeter Education Authority and the Department of Scientific and Industrial Research.

*Washington Singer Laboratories,
University College of the South West,
Exeter.*

ELECTRIC DISCHARGES IN LIQUIDS. PART II. THE ARC DISCHARGE IN WATER (CONTINUED).

BY HERBERT DYSON CARTER, M.Sc., AND ALAN NEWTON CAMPBELL,
D.Sc., Ph.D., F.I.C.

(Received 23rd May, 1932.)

In an earlier paper (Part I.)¹ we discussed the products of, and the reactions in the low tension arc discharge in water, with carbon and metal electrodes. Further investigations of the mechanism of the reactions are outlined here. In all cases the discharges employed were of the same type as that previously described, and particular attention was paid to the conflicting "thermal" and "electrical" reaction theories.

1. Energy Relationships.

In 1911 Makowetzky² conducted a study of the effects of the glow discharge on water vapour, including "the relations between current and energy consumed"; Shipley and Goodeve³ have made detailed

¹ Carter and Campbell, *Trans. Far. Soc.*, **28**, 479, 1932.

² Makowetzky, *Z. Electrochem.*, **17**, 217, 1911.

³ Shipley and Goodeve, *Eng. Jour. Canada*, **10**, 3, 1927; *Can. Jour. Res.*, **1**, 305, 1929.

investigations of the energy consumed by high voltage A.C. arcs in electrolytes. There has, however, been no attempt to relate the energy input in discharges to the chemical and heat energies evolved, and it was considered most important to measure these factors in under water arcs because of the large amounts of heat energy evolved relative to the electrical input.

It was found that the ammeter and voltmeter were not suitable for power measurements over any considerable time interval, because of the rapidity with which the current and arc potential changes. When the electrodes are shorted there is a maximum, and when open a minimum current, and because of the very small length of the arc, fluctuations between these two limits are difficult to eliminate; it is impossible, even with 30 amperes current, to keep the discharge steady for more than fifteen seconds.

Recording voltmeters and ammeters can be obtained, but investigation showed that special construction would be necessary for accurate measurement of very rapid current and voltage changes; recording wattmeters present even greater difficulties. Numerous calorimetric methods were tested but found to be quite unsuitable, due to the number of variable factors; because of the low resistance of the arc at striking, the line voltage fluctuates considerably, and in addition to this the resistance of the discharge bears no fixed relationship to the voltage or current. With a steady load calorimeters can be employed to measure current, potential and wattage separately; but when the power varies over wide ranges, as in the case of the arc, the method is useless. This is due to the fact that all formulæ relating heat in an electrical circuit to the power may be reduced to a form containing the square of the current, so that over a period of time a calorimeter measures the square root of the mean square value of the current, a quantity that differs greatly from the true mean value, when the fluctuations are considerable. Furthermore, it is well known that the value of the product of the average current and potential in a circuit differs from the true average wattage by an amount which increases with the extent of the fluctuations from the mean throughout the period of measurement.

The arc discharge can, however, be kept steady for ten to fifteen seconds, during which time the current and voltage may be read on ordinary meters; hence if the heat energy evolved in such a short time can be measured, the energy relationships of the arc can be obtained. The basis of the method employed was the "constant flow" calorimeter of Callendar and Barnes,⁴ and the modified apparatus is shown in Fig. 1.

The arc operated in distilled water in the chamber A, the whole being raised to the boiling-point before each run by means of the A.C. electrical heating coil K. The steam produced passed through B to the heat exchanger and condenser tube D; this tube was of thin metal for rapid heat conduction, while the outer tube L was of glass. The cooling "calorimeter" water entered from the chamber H₁ and circulated around the copper wire spiral between the tubes D and L, passing out through the chamber H₂ to the vessel J. By means of the constant head device F and a fine screw control G a very constant flow of water could be obtained, the maximum variation being 3 c.c. over a period of several hours. The intake temperature was measured by the thermometer T₁, and the outlet temperature by T₂. The two chambers,

⁴ Callendar and Barnes, *Phil. Trans.*, 415 A, 1895.

H_1 and H_2 were designed so that the water circulation was efficient, and the thermometers were of the Beckmann type for maximum sensitivity and accuracy. Inasmuch as the water in the tube L did not exceed 20 c.c., it was changed every two seconds with a flow rate of 600 c.c. per minute. There was a slight lag in the response of the output thermometer T_2 , but this registered any change in the heat input rate in about three seconds, reaching a steady state in five to ten seconds.

There are numerous advantages to this method. With adequate insulation (not shown in the figure) there was almost no radiation because the difference in temperature of the intake and output water was only a few degrees, and this water surrounded the steam tube D; the liquid entered at a temperature slightly below that of the surroundings, and left a little above. The calculations do not involve the measurement of the water equivalent. A full discussion of the precision obtainable

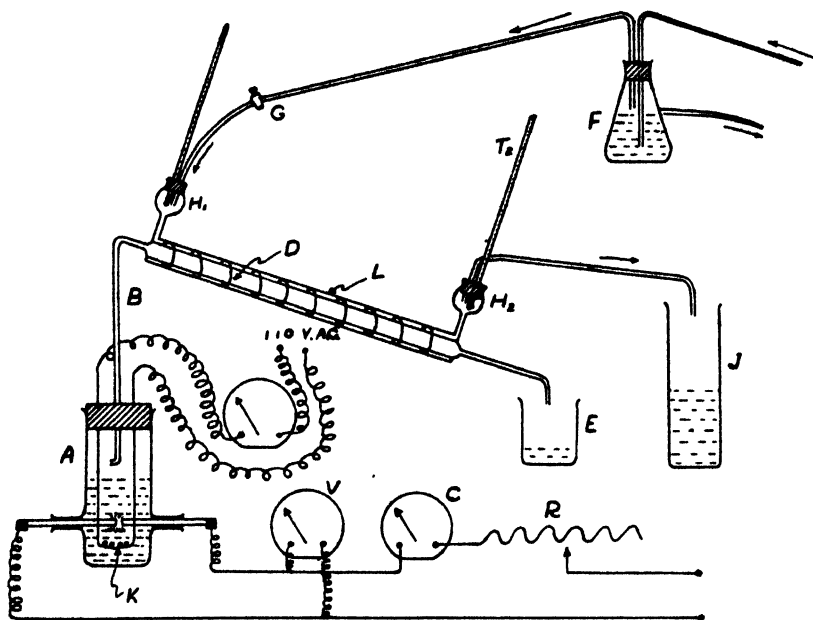


FIG. 1.

is given by Callendar and Barnes (*loc. cit.*), but the variation introduced here, namely the "steam calorimeter" principle, of necessity lowered the accuracy. The one correction introduced was the radiation loss of the chamber "A," which was, of course, well insulated; this factor was constant since the chamber was maintained at 100° C. regardless of the rate of energy input. The heat loss in this way was found to be 50 calories per minute for one type of Pyrex chamber; measurement was made by means of the heater K, supplied with a known quantity of electrical energy (direct current in this case). It was found necessary to maintain a flow rate through the calorimeter in excess of 300 c.c. per minute, since below this the circulation was unsteady.

Measurements can be made very rapidly. After the thermometers have become steady, and the water flow rate has been measured, the arc is operated steadily for fifteen seconds or longer and the current

and potential read on the meters. To complete the experiment it is only necessary to read the thermometer T_2 immediately the discharge breaks; the thermometer T_1 will remain steady to within 0.01° for several minutes, and need not be read immediately since it is unaffected by the steam flow. The range of the calorimeter may be adjusted either by altering the Beckmanns, or more conveniently, by changing the water flow rate.

A typical calculation will illustrate the method clearly. The arc with carbon electrodes was operated for fifteen seconds with 16 amperes at 25 volts, a total input rate of 5970 calories per minute. The difference in the readings of the two thermometers was 4.00° ; these had previously been compared by immersion in a constant temperature bath, and their constant difference found to be 3.40° , so that the total temperature difference during the run was 7.40° . The water flow rate was 780 c.c. per minute, giving the heat developed in the calorimeter by condensation of the steam from "A" at 5770 calories per minute. The heat from the cooling condensed water (cools from 100° to room temperature, giving up heat not imparted to it by the discharge) was 250 calories per minute, and that lost by radiation 50 calories per minute; the former quantity must be subtracted and the latter added, giving the net heat evolved as 5270 calories per minute.

Therefore approximately 700 calories per minute were "used up" by the discharge, in the chemical reactions; the radiant energy evolved could hardly have been appreciable, relative to this amount.

Regardless of the temperature of the discharge region, the reactions may be considered to take place at 100° , as far as the heats of reactions are concerned. With a gas of composition 60 per cent. hydrogen, 15 per cent. carbon dioxide and 22 per cent. carbon monoxide, and employing the accepted values of the reaction heats involved, the heat absorbed with a gas flow rate of approximately 700 c.c. per minute (S.T.P.) amounts to 460 calories per minute, the reactions being endothermal in their net effect.

We may conclude therefore, that apparently 240 calories per minute were not accounted for in the above calculation; this amounts to about 4 per cent. of the total input energy. It is not impossible that this is involved in the formation of the solid products, but more probably it is the result of errors in the assumed values of the reaction heats, the quantity of gas evolved and minor experimental errors. It is evident that only 12 per cent. of the input energy is converted into chemical energy, 88 per cent. being evolved as heat.

Experiments with different input energy rates gave similar results; in some cases, however, there was practically no energy missing, indicating that while the reactions are no doubt slightly endothermal, the heat absorbed is a small fraction of the input energy. Almost within the errors of the experimental method employed, the simple chemical reactions accounted for the observed energy relationships.

2. Current, Potential and Energy Relationships.

In the last three years there has been a widespread effort to relate the current factor to the reactions taking place in various discharges; Linder,⁵ Bodenstein,⁶ Brewer and Westhaver⁷ and others claim that

⁵ Linder, *Physic. Rev.*, **36**, 1375, 1930.

⁶ Bodenstein, *Chem. Revs.*, **7**, 2, 215, 1930.

⁷ Brewer and Westhaver, *J. Physic. Chem.*, **34**, 554, 1930; **34**, 153, 1930; **33**, 883, 1929.

definite relationships have been established for several reactions. Wansbrough-Jones⁸ and Lozier⁹ have demonstrated that certain minimum potentials, corresponding to the formation of definite ions, must be applied before reactions take place.

Because of the instability of the under water discharge with carbon electrodes, current and potential measurements had to be made simultaneously, at the same time recording the reaction rate. A sensitive flowmeter, of the type discussed by Benton,¹⁰ was employed to measure

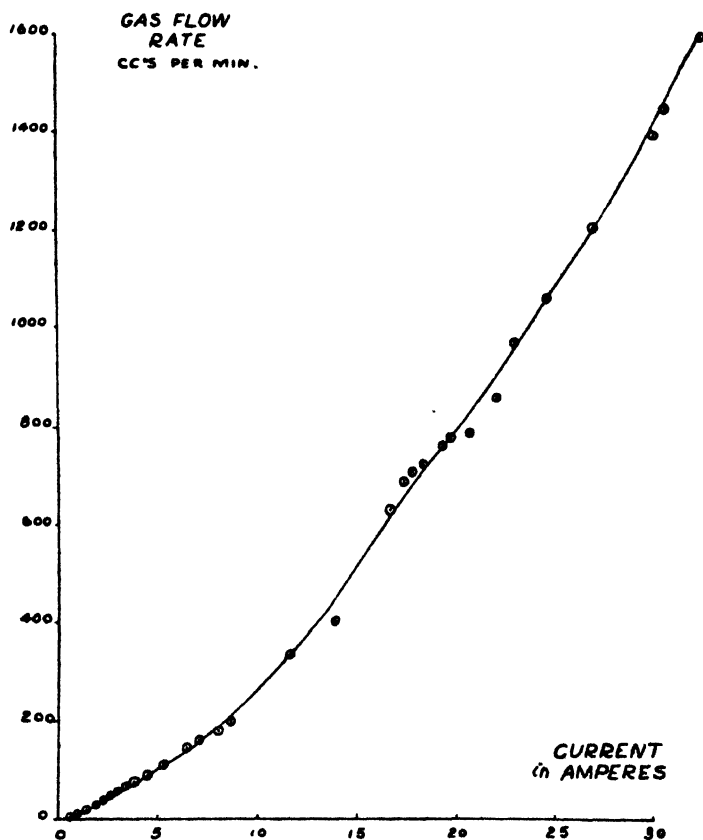


FIG. 2.

the rate of production of gases. Measurement of this factor was permissible since the water was kept vigorously boiling at atmospheric pressure and all other conditions were maintained constant.

(a) The effect of the current upon the reactions was determined with considerable accuracy since the voltage of the under water carbon arc can be kept constant to within 1 volt, by proper manipulation and control of the length of the discharge. The line resistance was altered to give currents from about 1 to 32 amperes, the voltage being constant at approximately 25 to 26 volts. The electrodes were of soft carbon,

⁸ Wansbrough-Jones, *Proc. Roy. Soc.*, 127, 806, 1930.

⁹ Lozier, Letter to Editor, *Physic. Rev.*, 36, 1417, 1930.

¹⁰ Benton, *J. Ind. Eng. Chem.*, 11, 623, 1919.

copper plated to within 1 cm. of the arc so that the current was conducted with negligible loss to the discharge region, and potential falls along the electrodes were eliminated.

The results are represented graphically in Fig. 2. A marked relationship between the gas flow rate and the current is exhibited, and the curve slopes slightly towards the vertical axis, *i.e.*, it is not linear.

(b) By keeping the line resistance constant and varying the length of the discharge it was found possible to vary the potential over a considerable range; the current, however, also changed with the voltage, and could not be kept constant. It was found that no voltages between 4 and 20 volts (approximately) could be obtained, since the discharge will not take place below the latter potential; at 4 volts there is no true arc, and this corresponds simply to a high resistance contact between the two electrode ends, giving a very small gas flow as Table I. shows.

It is obvious that there is no relationship between the reaction rates and the applied voltage. Nor does the input wattage appear to affect the gas flow, provided the current is constant and a true discharge is passing; the wattage is almost directly proportional to the voltage. The existence of a voltage range in which the arc will not strike has been definitely established; the

TABLE I.

Discharge Current. (Amperes.)	Discharge Potential. (Volts.)	Input Wattage. (Watts.)	Rate of Gas Flow. (c.c./minute.)
8.5	40	340	332
8.7	44	382	300
9.0	45	405	350
10.2	24	245	270
10.3	23	236	282
10.4	22	229	192
10.4	25	260	270
11.0	22	242	275
12.5	4	50	8
12.8	4	52	10

exact "critical potential" has not yet been determined however, but it is much higher than in the case of the air arc with the same electrodes. With a potential of 6 volts only intermittent sparking action can be secured, and with 30 amperes current (180 watts input energy) the gas flow rate is less than 25 c.c. per minute; when the potential is raised to 25 volts, and stable arcing secured, the gas flow rate increases to about 700 c.c. per minute with 20 amperes current (500 watts). Such marked influence upon the discharge reactions is only observed in the narrow range of the "critical potential" however, and not in the voltage ranges above or below this. Work is now being carried out to determine whether or not the operation of the arc is dependent upon the production of any definite ion or ions.

3. Anode and Cathode Reactions.

(a) With direct current it was observed that the cathode wore away at an inappreciable rate relative to the anode, and to verify this a series of quantitative tests were made. Short carbon rods were employed and a uniform drying procedure adopted in which after each run the rods were heated at 150° for ten minutes, and then dried over sulphuric acid for one hour before weighing. The flocculent precipitate (assumed to be 70 per cent. carbon as determined previously) was filtered off, and the hard granular carbon "dust" removed separately, both being dried

and weighed. The volume of gas evolved was measured, and the weight of carbon in it determined by analysis. The one remaining source of carbon, namely, the soluble compound formed, was not investigated, since experiment showed that the amount concerned was very small. The results are given in Table II. :—

TABLE II.

Carbon in Gases. (gm.).	Carbon in Compound. (gm.).	Granular Carbon. (gm.).	Total Carbon. (gm.).	Anode Loss. (gm.).	Cathode Loss. (gm.).
0.276	0.060	0.002	0.338	0.240	0.001
0.360	0.010	0.005	0.375	0.320	0.025
0.380	0.134	0.181	0.695	0.742	0.030
0.345	0.105	0.163	0.613	0.575	0.085
0.923	0.120	0.244	1.287	1.402	0.120

It is obvious that the chemical reactions involving carbon all take place on the anode; the small loss in weight of the cathode is no doubt due to mechanical loss of carbon particles ("granular carbon" in Table II.) and the data for the longest test in which the cathode lost 0.12 gram compared to 1.4 grams anode loss, indicates this, assuming that the two electrodes lose equal amounts in this way.

(b) The "uni-electrode" nature of the reactions involving the electrodes were further studied by substituting metallic rods for one of the carbons. With a copper anode and carbon cathode a stable arc can be obtained, but the volumes of gas evolved are much smaller than with two carbon electrodes. With a copper anode, however, large amounts of the characteristic green, flocculent, hydrated compound and none of the carbon compound are formed, just as when two copper electrodes are used.

When the polarity is reversed, that is with a copper cathode and carbon anode, the arcing is much more vigorous and the gas flow rate practically the same as with an ordinary carbon discharge; furthermore the usual amounts of the flocculent carbon compound, and none of the copper compound are produced.

The results were even more definite with iron electrodes. With this metal it was found that "steel wool" gave very stable arcing under water, probably because of the size of the strands; the high heat conductivity of metal rods and their tendency to weld together, makes them unsuitable for arcing in liquids, and fine wires or ribbons are more satisfactory. With an iron anode and carbon cathode a small gas flow was obtained, but large amounts of a reddish brown flocculent compound were formed. This was definitely identified as ferric hydroxide, in confirmation of our previous statements regarding hydroxide formation in these discharges.¹ With an iron cathode and carbon anode only the carbon compound was observed, but the gas flow rates were much greater.

Data from the analyses of the gases evolved in these tests are given in Table III.; the last two columns contain the volumes of oxygen actually found and the volumes corresponding to the hydrogen obtained. It is seen that with metallic anodes there is a large excess of hydrogen in the gases, the missing oxygen being undoubtedly in the solid compounds.

TABLE III.

Electrode Polarity.	Carbon Dioxide. Per Cent.	Carbon Monoxide. Per Cent.	Hydrogen. Per Cent.	Oxygen.	
				Actual. Vols.	Theoretical Vols.
Cu (+) C (-)	12.8	19.0	60.5	22.3	30.2
Cu (-) C (+)	13.0	25.0	59.5	25.5	29.7
Fe (+) C (-)	9.8	14.3	75.5	15.9	37.5
Fe (-) C (+)	14.6	20.0	63.2	24.6	31.6

4. The Composition of the Gases.

(a) An increase in the energy supplied to the discharge, due to either current or potential increases, raises the temperature of the arc considerably; 30 amperes will give approximately 3500°, compared to about 2500° at 15 amperes, as we have recently shown, the temperatures being measured by means of an optical pyrometer. The effects of such temperature increases upon the gas composition were determined by varying the current in a carbon-carbon arc. The results given in Table IV. do not contain the temperature measurements, however, as these were not sufficiently accurate to be useful; it may only be said that the last, or 27 ampere values correspond to a temperature about 1000° C. higher than the first, or 3.5 ampere values. There is a definite change in the proportion of carbon dioxide and monoxide in the evolved gases as the temperature is altered.

TABLE IV.

Discharge Current. (Amperes).	Carbon Dioxide. Per Cent.	Carbon Monoxide. Per Cent.	Hydrogen Per Cent.	Ratio CO/CO ₂ .
3.5	10	27	56	2.7
10.0	13	23	58	1.3
19.0	16	22	61	1.4
27.0	17	20	70	1.3

(Discharge Potential constant at 25 volts.)

(b) The temperature of the discharge is appreciably altered by the temperature of the surrounding liquid, as has been shown;¹ the corresponding effect upon the composition of the gases is given in Table V., the tests being made with constant current and voltage.

TABLE V.

Water Temperature. °C.	Carbon Dioxide. Per Cent.	Carbon Monoxide. Per Cent.	Hydrogen. Per Cent.	Ratio. CO/CO ₂ .
5	9	29	60	3.2
100	13	23	59	1.8

With the water at the boiling-point the discharge temperature is about 1000° higher than when operated in water at 5° , and this may be the cause of the alteration in the gas composition shown above.

5. Discussion

Before considering the mechanism of the chemical changes it is advisable to emphasise the purely physical effect of the liquid in which the discharges are operated; for it has been shown that over 85 per cent. of the electrical energy is spent in heating the water. It has been previously reported¹ that pressures up to 20 atmospheres have no effect upon the rate of the chemical reactions, and therefore do not affect the rate at which heat is given to the water by the arc. Considering the water to be at 0° C., 20 atmospheres pressure raises the boiling-point to 225° , or 125° above the normal temperature. It is obvious, therefore, that the temperature of the water relative to its boiling-point has no effect upon the rate of heat transfer.

It is almost certain that the heat is transferred from the very hot discharge region to the water by means of a steam film, and the most important factor involved is the latent heat of vaporisation, and not the heat required to raise the liquid to the boiling-point. Both these quantities must be considered however. In the case of water, the total heat required to raise a gram of liquid at 0° to the boiling-point, and vaporise it, remains almost constant as the boiling-point is raised. For example the heat required to vaporise a gram of water at atmospheric pressure and originally at 0° is approximately $100 + 540$, or 640 calories; at 20 atmospheres the amount of heat required is $225 + 446$, or 670 calories. The marked drop in the heat of vaporisation accounts for this coincidence.

In the under liquid arc discharge the rates of the chemical reactions are governed to a great extent by the physical condition of the medium, so that a study of these rates can be of little value in establishing the mechanism of the reactions taking place unless the condition of the medium be rigidly controlled. In this regard these discharges are distinct from those taking place entirely in gaseous media, or those in which the heat energy evolved is a small part of the input energy, for in the latter cases pressure and temperature effects are chemically significant.

A considerable amount of evidence has been collected indicating that the chemical reactions taking place in the low tension arc discharge in water are not of a "thermal" nature; by this term is meant either the thermal dissociation of water vapour, or the direct reaction of carbon with water vapour at a high temperature. Bjerrum¹¹ has shown that in the region 2000° to 3000° a rise in temperature of 500° results in an increase of 400 per cent. in the dissociation of water vapour. We have recently shown¹ that a rise of 1500° in the mean arc temperature (obtained by alteration of the water temperature) results in less than 50 per cent. increase in the rate of flow of the evolved gases; it is hardly probable, therefore, that the thermal dissociation of water vapour plays an important part in the discharge reactions.

It is possible that the carbon reacts directly with the steam, but the data indicate that this is not a major reaction. Langmuir¹² and Thiele

¹¹ Bjerrum, *Z. physik. Chem.*, **79**, 513, 1912.

¹² Langmuir, *J. Am. Chem. Soc.*, **37**, 1154, 1915.

and Haslam¹³ have shown that the carbon-steam reaction is complex and that at least five reactions are possible; it has been definitely established, however, that as the temperature is raised more carbon monoxide and less dioxide is formed. This follows from the so-called "water-gas" reaction equilibrium, involving the two carbon oxides, steam and hydrogen. At high temperatures such as exist in the discharge the equilibrium would be reached in an extremely short time, but the results given in Section 4 show that raising the temperature of the discharge, by raising the water temperature or the input wattage, definitely decreases the carbon monoxide content, with corresponding increase in the dioxide. This is in direct opposition to the thermal theory.

It must be noted that Haber¹⁴ has presented facts which seem to indicate that the value of the equilibrium constant for the water gas reaction is:—

$$K = \frac{P_{\text{CO}} \times P_{\text{H}_2\text{O}}}{P_{\text{H}_2} \times P_{\text{CO}_2}}$$

changes sign at some temperature in the region 3000° to 4000° C. The data is conflicting however, and there does not seem to be any recent reference to this in the literature. If the change of sign is an actual fact, then the alteration of the carbon oxide proportions discussed above could be used to support the thermal theory, for the variation of the ratio CO/CO₂ would be opposite to that found at temperatures below 3000°. Peters and Kuester¹⁵ recently studied the water gas reaction in an electric discharge tube at moderate temperatures, and found that the "equilibria" obtained were very different to those predicted by the thermal theory.

The curve in Fig. 2 lends strong support to the "electrical" theory, for according to modern theory a direct dependency upon current is to be expected with discharge reactions, provided that the potential employed is well over the critical ionisation potential. Furthermore the reaction rates are independent of the input wattage if the current is constant, despite the fact that the discharge temperature depends upon this factor. Shipley and Goodeve⁸ reported gas volumes produced by high tension arcs in water up to five times the amount predicted by Faraday's law; with the low tension arc and carbon electrodes there is a much greater discrepancy. Recent work with many types of discharges has shown that there are usually several ions produced in the reaction regions for each electron reaching the anode; and since there is a simple relationship between the ions produced and the molecules decomposed, no agreement with Faraday's law could be expected. Work is now being done to determine the maximum decomposition possible per electron in the arc circuit.

The fact that the reactions involving the electrodes and the oxygen from the water all take place on the anode is probably very significant. It is known that the anode in the carbon arc has a more extensive region of high temperature than the cathode, so that the "thermal" theory would explain this uni-electrode phenomenon. The results with metal-carbon arcs, however, show that the oxidation of the anode takes place even when it is the cooler of the two electrodes, that is when the anode

¹³ Thiele and Haslam, *J. Ind. Eng. Chem.*, **19**, 882, 1927.

¹⁴ Haber, *Thermodynamics of Technical Gas Reactions*, translation by Lamb, 1908, p. 135.

¹⁵ Peters and Kuester, *Z. physik. Chem.*, **148A**, 284, 1930.

is metallic and the cathode carbon, with production of the "hydroxidic" compounds discussed in an earlier paper.¹ A considerable transference of oxygen, or OH particles, to the anode seems to be indicated, and work is now proceeding with a view to obtaining more evidence in this connection. The data from metal-carbon arcs is not conclusive, since under water discharges with metal electrodes are very unstable and appear to be unlike the carbon arcs; such differences are easily explained by considering the heat conductivity of metallic rods, and the low electrical conductivity of the oxide layers which form. The fact that the oxides of carbon are gaseous (with the possible exception of the flocculent compound obtained in the under water discharge) may explain the stability of the arc, these oxides providing an extensive gaseous mantle. Linder⁵ considers that practically all discharge reactions take place in the neighbourhood of the cathode, but this point of view does not conflict with the fact that the oxidation takes place entirely at the anode of the under water arc; the decomposition of the water, and not the subsequent union of the oxygen or OH particles with the electrode material (such particles possibly migrating to the anode) is the important reaction according to the electrical theory.

Linder⁵ reviews the evidence concerning the dissociation of water vapour in the glow discharge and shows that the formation of OH particles or ions is a fundamental reaction. Bonhoeffer and Pearson¹⁶ studied this subject very fully, and conclude that the primary process is the formation of "activated" OH radicals, the life of which is, however, only about 1/1000 second. It is quite possible, therefore, that hydroxides of the arc electrode materials are produced by direct combination of activated or ionised OH particles produced by dissociation of the water, with the anode; considering the very short length of the arc and the velocity of the particles in it, the short life of the OH particles mentioned in the above paper would not seem to discredit this theory.

Abstract.

A constant flow calorimeter is described for rapid measurements of the heat evolved by the low tension arc discharge with carbon electrodes, operating in water; results with this device indicate that the reactions taking place may be slightly endothermal, but a large part of the input energy is expended in heating the water. Definite relationship between the discharge current and chemical reactions has been found, but above a certain critical potential the voltage does not affect the discharge; with a constant current the input wattage has no effect. The chemical reactions which were discussed in an earlier paper are shown to take place entirely on the anode, and further indication of hydroxide formation was obtained. The composition of the gases was altered by raising the discharge temperature, in a manner contrary to that predicted by the "thermal" theories; the contradictory evidence regarding the "water gas" equilibrium at high temperatures is noted. The physical effects of the liquid medium are discussed and the mechanism of the chemical reactions reviewed in the light of recent work on electric discharges.

*Chemistry Department,
University of Manitoba.*

¹⁶ Bonhoeffer and Pearson, *Z. physik. Chem.*, **14B**, **1**, 1931.

THE SORPTION OF CONDENSIBLE VAPOURS BY POROUS SOLIDS. PART I. THE APPLICABILITY OF THE CAPILLARY THEORY.

BY A. GRAHAM FOSTER.

Received 18th May, 1932.

The publication of a series of accurate measurements of equilibria between dehydrated gels (silica gel, and ferric oxide gels) and condensible vapours (water, benzene and ethyl alcohol) by Lambert and his collaborators,* affords more reliable data than have hitherto been available for a theoretical consideration of this aspect of sorption.

The pressure concentration equilibria of seven systems have now been determined isothermally at different temperatures. Five of these systems show hysteresis phenomena which are associated with real equilibrium conditions; the isothermals differ fundamentally in shape from those of the two systems which do not exhibit hysteresis, and resemble the curves obtained by Anderson¹ in his experiments with silicic acid gels, which formed the basis of Zsigmondy's "Capillary Theory" of sorption.²

There can be no doubt that capillary condensation plays an important part in the sorption processes of some porous solids, although there now appears to be no justification for the view expressed by Patrick,³ that the sorption of vapours by such solids is entirely due to condensation. The object of this paper is to show that the conception of capillary condensation as a secondary process, following layer adsorption, provides a simple explanation of those types of isothermals which exhibit hysteresis.

The Effect of Temperature on Sorption Equilibria.

According to the capillary theory, the vapour pressure of the sorbed liquid is determined quantitatively by the Kelvin equation, which may be written in the following form:—

$$R \cdot T \cdot \ln \frac{p}{p_s} = \frac{2 \cdot M \cdot S}{d \cdot r},$$

where p is the equilibrium pressure,
 p_s the saturation pressure,
 M the molecular weight,
 S the surface tension, and
 d the density, of the sorbed liquid at T Abs.

* Studies of Gas-Solid Equilibria.

Part I. Lambert and Clark, *P.R.S.*, 117 A, 183, 1927.

Part II. Lambert and Clark, *P.R.S.*, 122 A, 497, 1929.

Part III. Lambert and Foster, *P.R.S.*, 134 A, 246, 1931.

Part IV. Lambert and Foster, *P.R.S.*, 136 A, 363, 1932.

(These are referred to as Part I, etc., throughout the present paper.)

¹ Anderson, *Z. physik. Chem.*, 88, 191, 1914.

² Zsigmondy, *Z. anorg. Chem.*, 71, 356, 1911.

³ Patrick, *J.A.C.S.*, 42, 946, 1920; *J. Physic. Chem.*, 29, 601, 1925.

r denotes the radius of the space in which condensation occurs, and for a given adsorbent is determined solely by the volume of liquid contained in the pores. For a constant volume of sorbed liquid, the following relation should therefore hold:—

$$R \cdot T \cdot \ln \frac{p_s}{p} = K \cdot \frac{S}{d}$$

The term on the left represents the adsorption potential, and should decrease as the temperature increases. The temperature effect during capillary condensation will thus differ from that during layer adsorption, when, according to Polanyi,⁴ the potential at constant volume is independent of the temperature. It is, therefore, possible to obtain some

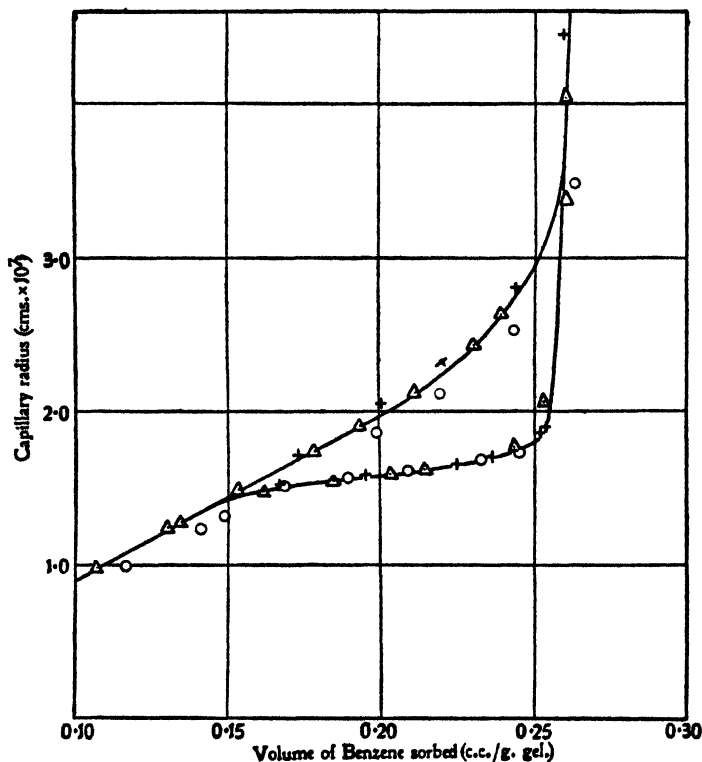


FIG. 1.— + 40° C.; △ 50° C.; ○ 60° C.

information about the mechanism of the sorption process by examining the isothermals of a given system at different temperatures.

The following figures, derived from the isothermals for benzene on ferric oxide gel (Part II.) show that the potential actually decreases with temperature in accordance with the Kelvin equation. The first column shows the values of the potential (e) at different temperatures corresponding to a constant sorbed volume (0.22 c.c. per gm. gel) on the descending curves in the hysteresis area. The second column gives the values of the function S/d to which the potential should be proportional, whilst the final column shows the values of the product $e \cdot d/S$, which should be

⁴ Polanyi, *Verh. deut. physik. Ges.*, 18, 55, 1916.

constant. The agreement is very close, being within one-half of 1 per cent., and is found with other points on the descending isothermals. The ascending points show no such agreement and the variation of potential with temperature during addition is small.

TABLE I.

Tempr. °C.	Adsorption Potential, (<i>e</i>) . cals. p. gm. mol.	<i>S/d</i> .	<i>e. d/S</i> .
40	670	29.68	22.57
50	645	28.52	22.62
60	616	27.31	22.55

The effect of temperature on the equilibrium in the hysteresis area is best illustrated graphically by plotting the capillary radius against the volume of sorbed liquid. These "radius-volume" curves are derived from the pressure concentration isothermals by calculating the radius from the observed equilibrium pressure by means of the Kelvin equation. From the corresponding concentration the volume is calculated, assuming the normal value for the liquid density.

Fig. 1 shows the radius-volume curves for benzene on the normal ferric oxide gel, and corresponding curves for alcohol on the same gel are shown in Fig. 2.

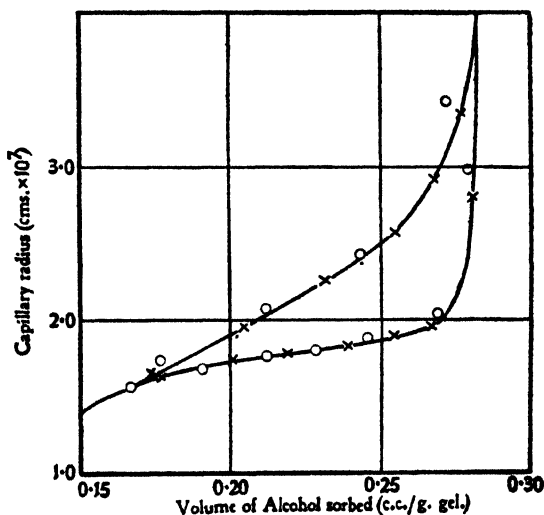


FIG. 2.—○ 60° C.; × 70° C.

In both systems the descending curves coincide over the hysteresis areas, but the ascending curves do not, and the hysteresis loop becomes slightly smaller as the temperature increases. The water silica gel system (Part III.) behaves in a similar manner. The radius-volume curves have not been drawn, but the variation of potential with temperature agrees with the Kelvin equation. For a sorbed volume of 0.16 c.c. per gm. gel on the descending isothermals at 60° C. and 70° C., the respective potentials are 561 and 550 cal. per gm. mol. The ratio of these is 1.020, whilst the ratio of the corresponding values of S/d is 1.022.

Isothermals for benzene and alcohol have also been determined on a different sample of ferric oxide gel, the "water-treated" gel, described in Part IV. The radius-volume curves for alcohol on this gel are shown in Fig. 3. The descending points at 40° C., 50° C. and 60° C. all lie on a smooth curve, but the ascending points are irregular. Fig. 4 shows

similar curves for benzene on the same gel. In order to avoid confusion the descending points at 50° C. and 60° C. only are shown, the irregular

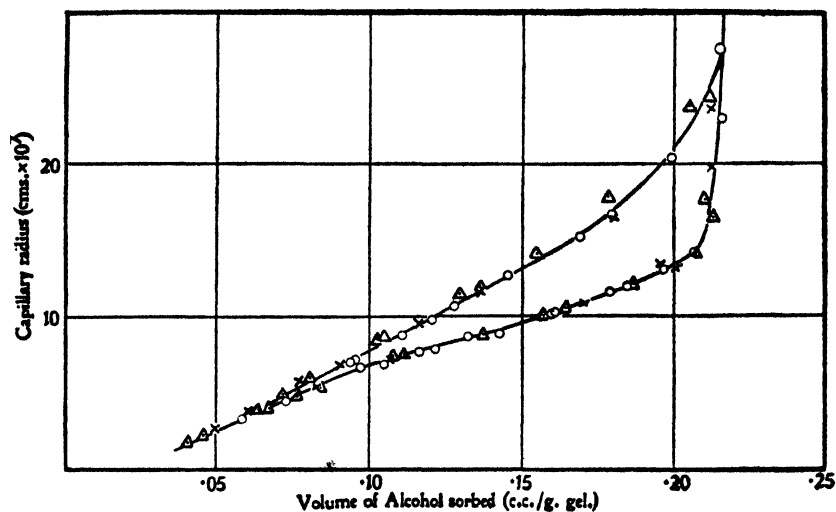


FIG. 3.—△ 40° C.; × 50° C.; ○ 60° C.

ascending points being omitted. In this system there is a slight but definite shift of the curves towards the right as the temperature increases, but there can be little doubt that this is due to the fact that the saturation

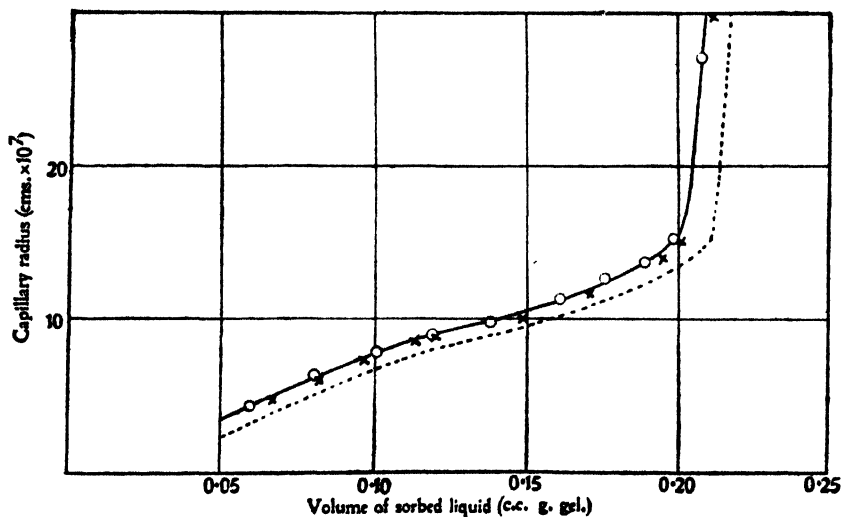


FIG. 4.—○ 50° } benzene;
× 60° }
..... alcohol.

volume does not remain constant, as in the other systems, but increases with temperature. The 50° C. curve can be made to coincide with the 60° C. curve by displacing it horizontally away from the r axis by an

amount equal to the difference in the saturation volumes at these temperatures.

In the hysteresis areas of all five systems examined, the effect of temperature on the desorption equilibria is in close agreement with the Kelvin equation, and it is possible to reduce isothermals at different temperatures to the same scale by plotting them as radius-volume curves. The radius-volume curve, for a given adsorbent, should be determined solely by the size and distribution of the pores, and it should be possible, once this has been derived from a single isothermal, to calculate, by means of the Kelvin equation, the equilibria for any other liquid at a given temperature, provided that the necessary physical constants are known. There are, however, several difficulties which have to be considered before this can be accomplished, and these are best illustrated by a comparison of the curves for alcohol and benzene on the two types of ferric oxide gel.

Comparison of Isothermals for Alcohol and Benzene.

If the internal volume of the adsorbent remains constant, the volume of liquid taken up at saturation should also be constant, and at intermediate stages of the condensation process equal volumes of different liquids should fill the pores to the same extent, so that the radius volume curves derived from isothermals for all liquids on a given adsorbent should coincide. Actually the curves for benzene and alcohol do not coincide, and the discrepancy is partly due to the fact that the saturation volume does not remain constant and both gels take up more alcohol than benzene. This behaviour is also shown by silica gel, where hysteresis is absent (Part III.), and was also observed by Anderson. The following figures illustrate this variation of the saturation volume:—

TABLE II.

Adsorbent.	Saturation Volume (c.c. per gm. of gel).	
	Alcohol.	Benzene.
Ferric oxide gel (normal) . .	0.284	0.274
Ferric oxide gel (water-treated) . .	0.215	0.205
Silica gel (Part III.) . .	0.218	0.203
Silica gel (Anderson) . .	0.568	0.553

A comparison of Figs. 1 and 2 shows that the hysteresis area begins at a lower volume with benzene than with alcohol, and that the volume of liquid taken up by condensation is the same in both cases. The additional amount of alcohol must therefore be present in the adsorbed layer before condensation occurs.

In addition to this volume effect, there is another factor which must be considered when comparing the behaviour of different liquids on a given adsorbent. The radius calculated from the Kelvin equation is less than the true radius of the pores by an amount equal to the thickness of the adsorbed layer, which will vary according to the size of the adsorbed molecules. For this reason, even if the Kelvin equation were valid for such small radii as are found for the normal ferric oxide gel, it

is not to be expected that the values calculated from isothermals for different liquids will show an exact agreement, except in favourable circumstances, as for example, when the adsorbed molecules happen to be of the same size, or when the pores are so large that the difference in layer thickness is negligible.

A close examination of the two series of radius-volume curves for alcohol and benzene shows clearly how the variation of the saturation volume and the layer thickness affects the applicability of the Kelvin equation. It has already been mentioned that the curves for benzene on the water-treated gel show a slight shift away from the radius axis as the temperature increases, which is accompanied by a corresponding increase in the saturation volume. The dotted line in Fig. 4 represents the radius volume curve for alcohol, transferred from Fig. 3, and shows a similar but larger displacement, and a corresponding larger increase in the saturation volume. If the benzene curve is displaced horizontally by an amount equal to this difference in saturation volume, it very nearly coincides with the alcohol curve over the entire range. In these systems, therefore, the only disturbing factor appears to be the volume effect, and the difference in thickness of the adsorbed layer may be neglected in comparison with the capillary radius which is of the order twenty molecular diameters.

The radius-volume curves for benzene and alcohol on the normal gel (Figs. 1 and 2) are also similar in shape, and can be made to coincide by displacement. In addition to the horizontal displacement equal to the difference in saturation volume, a vertical displacement is also necessary since the radii calculated from the alcohol isothermals are slightly higher than those calculated from the benzene isothermals at corresponding points. The mean radius for alcohol is 1.8×10^{-7} cm., compared with 1.6×10^{-7} cm. for benzene; how far this actually represents a difference in the thickness of the adsorbed layer, is, however, uncertain. There are at present too many uncertain factors to enable any reliable information on this point to be derived from this series of experiments with only two liquids. The adsorbed layer may be one, two or more molecules thick; the effective size of the molecules is not known accurately, and must depend upon their orientation; further, it is not known whether the Kelvin equation is strictly valid when the calculated radii are so low. If the molecular diameters are calculated from the liquid density, and the layer assumed to be two molecules thick, the actual difference between the radii for alcohol and benzene should be about 0.15×10^{-7} cm., as compared with the observed difference of 0.20×10^{-7} cm.

In the absence of more extensive data it is not yet possible to discuss this problem further. Experiments are now in progress with other liquids on these gels, but the only results available are some isothermals for carbon tetrachloride on the normal ferric oxide gel, which have been determined by the dynamic retentivity method. These approximate figures indicate that the mean capillary radius in this system is about 1.6×10^{-7} cm., which agrees with the value for benzene.

It is known that the Kelvin equation cannot remain valid when the radius of curvature is of molecular dimensions, since the surface energy departs from its normal value. It is therefore probable that the calculated radii for the normal gel are too low, and that the lack of complete agreement between the values for different liquids is partly due to the fact that the limit of validity of the equation has been reached. The

water-treated gel, however, appears to have a mean capillary radius of the order 10^{-6} cm., and there is no reason why the equation should not be strictly valid for these large radii. Zsigmondy evidently considered that it held good for lower radii, since the values obtained by Anderson were about 2.5×10^{-7} cm., or about five molecular diameters. The values found here for the normal gel are still lower, being only about three diameters, but even if they are incorrect, the equation is still reliable for comparative purposes, as shown by the radius volume curves discussed above. The experiments of Crowther and Puri⁵ on the capillary structure of soils are of especial interest in this connection because they also indicate that, for comparative purposes, the Kelvin equation remains valid when the calculated radii are extremely low.

Distribution of Capillaries.

A comparison of Figs. 1 and 4 shows that in addition to the considerable difference in the magnitude of the capillary radius of the two ferric oxide gels, there is also a difference in the distribution. On the normal gel practically the entire condensation process takes place between the concentrations 0.15 and 0.25 c.c. benzene per gm. of gel, and over this range the radius changes very slightly, rising from 1.4×10^{-7} cm. to 1.8×10^{-7} cm. In contrast to this, the curve for benzene on the water-treated gel rises from a radius 4.0×10^{-7} cm. to 14×10^{-7} cm., whilst the sorbed volume increases from 0.05 to 0.20 c.c. per gm.

Both curves have a point of inflection near the middle of the flat part, above which they are convex to the volume axis and below which they are concave to it. The reason for this inflection becomes clear when the distribution of the capillaries according to their size is considered. A point on the radius volume curve denotes the volume of liquid V required to fill all the pores of radius equal to or less than the corresponding value of r . At this point the capillaries with greater radii than r are not yet filled, and the addition of a small amount of liquid dV will fill those having radii between r and $r + dr$, so that the curve obtained by plotting the tangents dV/dr against the corresponding values of r will show the extent to which pores of a

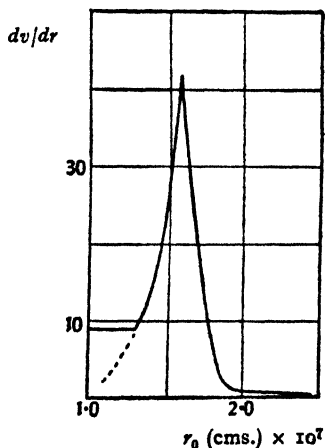


FIG. 5.

given radius contribute to the internal volume of the gel. The volume distribution curve so obtained from the radius-volume curve for benzene on the normal gel (Fig. 1) is shown in Fig. 5. The shape of this curve resembles that of the Gauss error function and shows that the pores are distributed according to the laws of probability. The corresponding curve for benzene on the water-treated gel has a lower and less abrupt peak.

The point of inflexion in the radius volume curves enables the mean radius to be defined quite sharply, and since there is a corresponding

⁵ Crowther and Puri, *P.R.S.*, 106A, 232, 1924.

point in the pressure concentration isothermals, it is unnecessary to plot the former in order to compare the calculated radii for different systems. Anderson compared his data for water, alcohol and benzene by calculating the radii at two badly defined points, the beginning of the hysteresis area and the so-called "opacity point." It is evidently preferable to calculate the values from the pressures at which the points of inflexion occur in the isothermals.

This distribution of uniform, non-intersecting, cylindrical capillaries is, of course, not an accurate representation of the gel structure, which must be much more complex if the pores are irregular spaces between colloid particles, the sizes of which are distributed according to probability. The application of the Kelvin equation, which is derived by considering the equilibrium of liquid in a uniform cylinder, thus leads to an equivalent structure of a simpler nature than the irregular structure actually filled by capillary condensation, but which has similar properties. The fact that the adsorbent may, for some purposes, be treated as a simple cylindrical structure enables some interesting calculations to be made.

For example, it is possible to obtain an approximate estimate of the thickness of the adsorbed layer by the following method. The point at which hysteresis begins should denote the completion of the layer adsorption process and the appearance of capillary condensation. The ratio of this concentration to the saturation value should therefore give the ratio of the volume of the adsorbed layer to the total internal volume of the adsorbent. The mean capillary radius calculated from the isothermals on the water-treated gel is 9×10^{-7} cm., and if the adsorbed layer were two molecules thick, the true radius of the pores would be 10^{-6} cm. A simple calculation shows that this layer would represent about 20 per cent. of the total volume, and that a layer one molecule thick would represent about 10 per cent. The actual concentrations at which hysteresis begins with benzene and alcohol are 22 per cent. and 21 per cent. respectively, of the saturation values, so that it would appear that the adsorbed layer is actually two molecules thick. A more exact method of calculation might lead to a higher surface volume ratio, since the surface of the adsorbent itself is more irregular than that of the adsorbed layer, but it is reasonable to suppose that the layer is not more than two molecules thick.

Heats of Sorption.

The fact that the effect of temperature is not the same on the ascending as on the descending equilibria, when hysteresis occurs, denotes that there is a corresponding difference in the heats of sorption. The differential heats of sorption calculated from the ascending isothermals are lower than those calculated from the descending curves, which are in agreement with Hückel's theory⁶ of the heat evolved in capillary condensation, and may be interpreted as heats of wetting. It is hoped to discuss these results in detail when more data are available.

Hysteresis.

In each of the five systems examined, the lower portion of the isothermals is completely reversible and the Kelvin equation is inapplicable in this region. The irreversible phenomena therefore appear to be

⁶ Hückel, *Adsorption und Kapillarkondensation*, Leipzig, 1928.

associated with the capillary condensation process which follows the reversible layer adsorption. According to Zsigmondy, the higher pressures observed during addition of vapour are due to incomplete wetting since the radius of curvature of the meniscus is greater when there is an angle of contact with the walls of the capillaries. The radius volume curves (Figs. 1 to 4), however, provide no evidence of any simple relationship between the radii at corresponding points on the two branches of the hysteresis area. If the walls are covered by the adsorbed layer before condensation begins it is difficult to see how the wetting equilibria can fail to be reversible.

In order that condensation may occur in a capillary, it is essential that the meniscus shall be formed. This process, however, cannot take place until there is sufficient liquid present to block the pore at its narrowest point. In seeking an explanation of hysteresis it is therefore necessary to enquire whether the phenomenon may not be due to some delay in the appearance of capillary condensation, after the completion of the adsorbed layer, owing to the lack of reversibility associated with the process of the formation and breaking of the meniscus.

At the beginning of the hysteresis area it is to be supposed that the surface of the capillaries is covered by a strongly adsorbed layer only a few molecules thick, and that the forces tending to form an additional layer are much smaller than those already operative, and are also smaller than those which would prevail if condensation occurred. The adsorptive forces become weaker as layer formation proceeds and molecules are held at a greater distance from the surface, but at the same time the space remaining in the centre of the capillaries becomes smaller, so that a point is reached at which the cohesive forces would be able to produce (by capillary condensation) a greater lowering of vapour pressure than the adsorptive forces. It is not necessarily possible for condensation to occur as soon as this point is reached, since the behaviour of a system as more vapour is added will depend upon the extent to which the adsorbed layer has filled the pores. In those which are already blocked at their narrowest points, and in which the meniscus has formed, condensation can proceed without delay; but in those which are not blocked, the meniscus cannot form until more liquid is present. This liquid must remain on the walls, where it will exert a higher pressure than would result if condensation occurred. Since the capillaries are of varying sizes, there must always be some liquid in this unstable state until all have been blocked at their narrowest points and the meniscus formed, after which the condensation process should proceed spontaneously. In all the systems examined there is actually a short range of concentration above the hysteresis area where the equilibria are reversible.

The equilibria during desorption are determined by the Kelvin equation, and it must be assumed that during withdrawal all the sorbed liquid is bounded by the meniscus (with the exception of the strongly adsorbed layer which remains on the walls). The higher pressures observed during addition must be attributed to the liquid which is held in an unstable state on the walls of those pores in which the meniscus has not formed, the pressure of which masks the progress of the condensation process. The ascending isothermals themselves give no indication of the amount of liquid so held, but it should be possible to obtain some information on this point by examining the effect of interrupting the smooth addition of vapour to a system by a withdrawal. The extent to which the pressure then falls within the hysteresis area

should give some indication of the distribution of the liquid. If only a small amount were originally present in the unstable state, the pressure ought to fall considerably towards the descending branch, but if a large amount were held on the walls and little condensation had occurred, the pressure should not fall far below the ascending branch. The behaviour of systems in the hysteresis area has not been studied very extensively, but the observations which have been made (with benzene on the normal ferric oxide gel, and water on silica gel) suggest that there may be a considerable difference in distribution during addition and withdrawal. It may be possible to obtain further information by examining the heats of sorption, which are appreciably lower during addition.

There is a close similarity between the hysteresis phenomena observed with vapours and those found in the palladium-hydrogen system,⁷ although there can be no doubt that the mechanism of the sorption process is fundamentally different. The resemblance is probably due to the fact that in both systems a small amount of gas or vapour is unable to enter the strongly bound state and exerts a higher pressure than the true equilibrium value, which is only observed during desorption, when the loosely bound gas or vapour is withdrawn first, and its disturbing effect eliminated.

The Shape of Sorption Isothermals.

The behaviour of systems which give reversible isothermals is in marked contrast to that of the systems which show hysteresis. The isothermals for benzene on silica gel are characteristic examples of the normal type, to which the Freundlich equation is applicable. This type of isothermal has been investigated extensively by other workers, notably by Coolidge⁸ and by Goldmann and Polanyi,⁹ who found that the adsorption potential (at constant volume) was independent of the temperature, in accordance with the Polanyi theory of layer adsorption. Fig. 6 shows the isothermals for benzene on silica gel plotted as potential-volume curves, which coincide over a wide range. There is no evidence that capillary condensation occurs in systems of this type, so that it must be supposed that the formation of the adsorbed layer fills the entire internal volume of the adsorbent, either because the pores of these adsorbents are smaller, or because the adsorbed layer is thicker, than is the case with adsorbents like ferric oxide gel.

The isothermals obtained with the water-treated ferric oxide gel evidently represent an extreme type which arises when the adsorbent has a coarse capillary structure. The mean radius of the pores, calculated from the Kelvin equation, is about twenty molecular diameters, and it is obvious that the formation of an adsorbed layer one or two molecules thick will account for only a small fraction of the total sorption. Consequently very few of the sorbed molecules will be in contact with the surface of the adsorbent or in any way influenced by it. The Kelvin equation is applicable over a wide range of concentration and the general shape of the isothermals is determined by the structure of the adsorbent.

The type of isothermal which exhibits an extreme deviation from the normal in the opposite direction arises when the pores are only a few

⁷ Lambert and Gates, *P.R.S.*, 108A, 456, 1925.

⁸ Coolidge, *J.A.C.S.*, 46, 596, 1924.

⁹ Goldmann and Polanyi, *Z. physik. Chem.*, 132, 321, 1928.

molecules wide and practically all the adsorbed molecules are in actual contact with the surface. Curves of this type have been investigated by McBain,¹⁰ who found that the sorption of some vapours by sugar charcoals took place at extremely low pressures and was in agreement with the Langmuir theory, showing that the formation of the first adsorbed layer filled almost the entire internal volume. In this, as in the opposite extreme case, the type of the isothermals appears to be determined primarily by the size of the pores, and the nature of the sorbed liquid has only a secondary influence.

The specific properties of the liquid have a very considerable effect in determining the shape of isothermals of intermediate types, as shown by the results obtained with silica gel. The difference in shape between the isothermals for alcohol and benzene is so marked as to suggest that the mechanism of the sorption process is different. It is essential to obtain more extensive data before attempting to advance an explanation of these results. There are

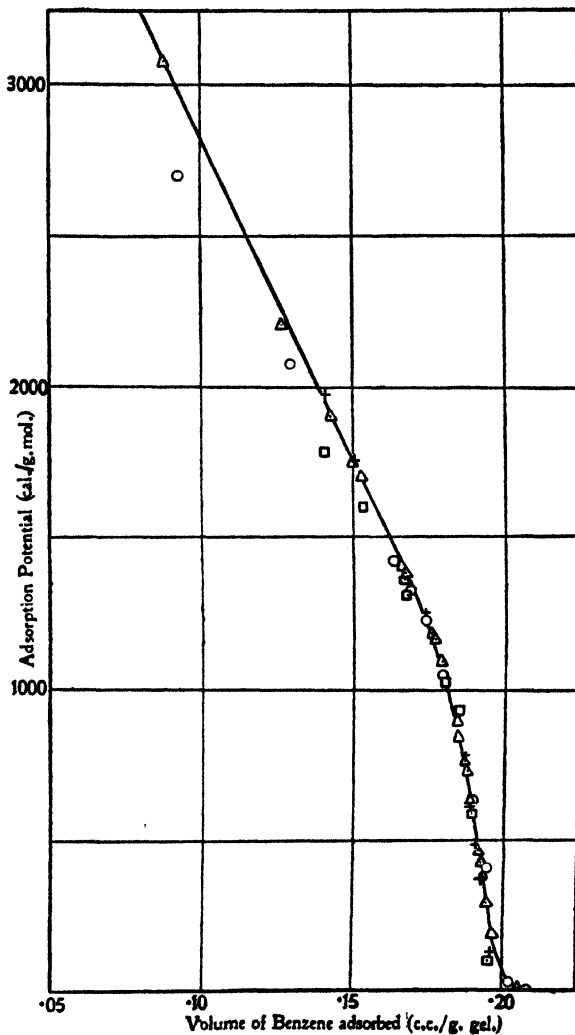


FIG. 6.—□ 15° C.; + 40° C.; △ 50° C.; ○ 70° C.

two points of interest which may, however, be mentioned in the present paper, since they suggest a possible explanation of the peculiar behaviour of water on silica gel.

The occurrence of hysteresis in the water silica-gel system denotes that condensation occurs towards the end of the sorption process. The

¹⁰ McBain, *J.A.C.S.*, **52**, 2668, 1930.

calculated radius is almost certainly too low, being only 10^{-7} cm., but it is interesting to consider what might happen in certain circumstances if it were correct. The water molecule is smaller than the alcohol or benzene molecule, and has a diameter of about 3.5×10^{-8} cm., compared with about 5.5×10^{-8} cm. for the latter. If the adsorbed layer of water present before condensation occurs is two molecules thick, the true radius of the pores of the gel will be about 1.7×10^{-7} cm. A similar layer of alcohol or benzene will be about 1.1×10^{-7} cm. thick, and the formation of such a layer will leave in the centre of the capillaries a space only about 0.6×10^{-7} cm. radius, which will not fill up by capillary condensation in accordance with the Kelvin equation and will represent only the last small fraction (about one-tenth) of the total sorption process. It is therefore possible, in small capillaries, for the size of the adsorbed molecule to determine the extent to which layer adsorption and condensation take place.

The water silica-gel system presents another anomaly which may be connected with the appearance of capillary condensation. The isothermals rise much more steeply from the concentration axis than those for alcohol or benzene; when the gel is half saturated with water, the pressure is about one-fifth of the saturation pressure, as compared with one-fiftieth for the other vapours. The forces tending to cause layer adsorption must therefore be much weaker for water than for alcohol or benzene, whilst the cohesive forces are of the same order of magnitude for all three liquids; it is thus more probable that the sorption process will be completed by condensation than by continued layer adsorption. The Kelvin equation may be applied to calculate the pressures which would result if alcohol or benzene were held by capillary condensation in pores of the same radius as that derived from the water isothermals. These pressures are appreciably higher than those at which the vapours are actually held by the gel, indicating that the adsorptive forces are greater than the cohesive forces, even towards the end of the sorption process. With water, the adsorptive forces become weaker than the cohesive forces as sorption proceeds, and the final stage is a condensation process.

A complete explanation of the behaviour of the silica-gel systems involves a knowledge of the specific nature of the adsorptive forces. It is clear that the behaviour of molecules during sorption is not completely defined by their critical constants, nor does there appear to be any direct connection with any particular physical property (such as the dielectric constant). It would appear necessary to consider the size and shape of the adsorbed molecules, as well as the size of the pores of the adsorbent, in any theoretical treatment of the problem. Further progress must for the present depend upon the accurate experimental investigation of isothermals, particularly those of abnormal types.

Summary.

An examination of recent experimental determinations of sorption isothermals of various types leads to the following conclusions:—

(1) The shape of sorption isothermals is determined largely by the actual size of the pores of the adsorbent. If they are small, the formation of a strongly adsorbed layer one or two molecules thick is sufficient to fill the entire internal volume, whereas if they are large the layer adsorption is followed by capillary condensation, until the pores are completely filled.

(2) Hysteresis appears to be associated with capillary condensation, but the explanation proposed by Zsigmondy is inadequate. It is suggested that the lack of reversibility is due to some delay in the formation of the meniscus during the addition of vapour to the system.

(3) When capillary condensation occurs, the Kelvin equation is applicable over the descending portion of the hysteresis area. The effect of temperature on the desorption equilibria is in exact agreement with this equation, which also enables isothermals for different liquids on the same adsorbent to be reduced to the same scale, by plotting the capillary radius against the volume of sorbed liquid. These radius-volume curves can be made to coincide by displacement parallel to the axes.

(4) In systems which give reversible isothermals, there is no evidence that condensation occurs. Isothermals of this type are to be attributed to layer adsorption, and the specific properties of the sorbed liquid have a considerable influence in determining their shape.

The author wishes to acknowledge the helpful criticism and advice which he has received from Dr. B. Lambert during the preparation of this paper.

*Old Chemistry Department,
University Museum,
Oxford.*

THE SYSTEM $\text{NiSO}_4\text{—CaSO}_4\text{—H}_2\text{O}$.

BY ALAN NEWTON CAMPBELL AND NICHOLAS SAMUEL YANICK.

Received 18th April, 1932.

It was observed by one of us (A. N. C.) that calcium sulphate is distinctly more soluble in hot nickel sulphate solution than in water at the same temperature. As increase in solubility in presence of a second salt is usually indicative of double salt formation, a phase rule study of the above system seemed desirable. It appears that no double salt is formed, but the curves are of a somewhat unusual form.

Experimental.

Purity of Reagents. NiSO_4 .—Mallinckrodt's $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, C.P. quality was used. According to the analysis supplied the maximum impurity was 0.10 per cent. of alkali salt, which is hardly likely to affect double salt formation.

CaSO_4 .—Gypsum was prepared in the following manner. Precipitated chalk (U.S.P.) was dissolved in pure hydrochloric acid, and warmed and filtered several times to remove silica. It was then precipitated with the calculated quantity of pure sulphuric acid and the gypsum obtained preserved under water, after washing acid free.

Analysis of the gypsum thus produced yielded the following impurities:—

SiO_2	Trace
Mg	0.05 per cent.
Fe	Trace
Ba	Absent.

In view of the well-known affect of particle size on solubility in the case of gypsum,¹ the finer particles were removed by suspending samples in water, stirring vigorously with a mechanical stirrer, and decanting the suspension. The residual samples thus obtained gave solubility values in water, agreeing well with those of Hulett and Allen.

Determination of Solubility.—Solubility determinations of the complete system at 45.0° , 75.0° , and 90.0° , were carried out in a thermostat the temperature variation of which was $\pm 0.05^\circ$. Saturated solutions of the appropriate solid phase were obtained by stirring mechanically for twenty-four hours, in accordance with the directions of Hulett and Allen. The solutions were filtered in an apparatus which is a modification of one previously described.² It is so convenient for its purpose that we subjoin a sketch.

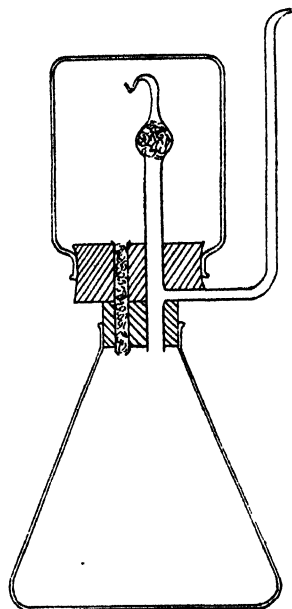


FIG. 1.

Saturated solution is produced in the bottle by stirring with appropriate solid phase for twenty-four hours in the thermostat. For this purpose the bottle is fitted with a mercury seal and glass stirrer. The mercury bung carrying the mercury seal is then removed and in its place the arrangement of double bungs and glass tubing, shown in the diagram, is fitted. Finally the conical flask, previously weighed, is fitted on the rubber bung. The whole is then inverted in the thermostat and conveniently kept in position by gripping it between the base and arm of a filter stand, loaded and suitably cut down.

Inversion of the apparatus causes filtration to take place, the side tube letting off the pressure produced in a high temperature bath, which otherwise blows the vessels apart. In the present research, although the apparatus proved admirable for the preparation of saturated solutions, the solid phase was left too wet for accurate analysis; it is well-known that gypsum absorbs large quantities of water. Accordingly, after removal of the saturated solution, it was necessary to resort to pressure filtration, which was also carried out in the thermostat in a small Buchner apparatus attached to a partially evacuated expansion chamber.

Analysis.—Nickel was first determined electrolytically and then calcium volumetrically with oxalate and permanganate. As a check on accuracy, some determinations of solubility of nickel sulphate and of calcium sulphate respectively in water alone were made. The figures obtained are given in Table I, which expresses the solubilities of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ in grams of NiSO_4 and CaSO_4 respectively per 100 grams water.

The solubilities in mixed solutions were then determined; many of the determinations were made in duplicate with excellent agreement.

As the solubility of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ is under all circumstances so small,

¹ Cf. Hulett, *Z. physik. Chem.*, **37**, 388, 1901; Hulett and Allen, *J.A.C.S.*, **24**, 667, 1902.

² *J.C.S.*, 179, 1930.

TABLE I.

Temperature.	$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$.	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$.
45.0°	48.36	—
45.0°	—	0.211
75.0°	60.30	—
75.0°	—	0.199
90.0°	68.70	—
90.0°	—	0.177

it was not thought feasible to saturate with NiSO_4 solutions unsaturated with respect to CaSO_4 . For all solutions, therefore, the added solid phase present in excess was $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, except at the point of inflexion where both solid phases were present in excess. The results are expressed in Table II, in grams, as before, of anhydrous salt per 100 grams water.

TABLE II.

Solution.			Solid Phase.		Solution.			Solid Phase.	
Temperature, °C.	Solubility, NiSO_4 .	Solubility, CaSO_4 .	Per Cent., NiSO_4 .	Per Cent., CaSO_4 .	Temperature, °C.	Solubility, NiSO_4 .	Solubility, CaSO_4 .	Per Cent., NiSO_4 .	Per Cent., CaSO_4 .
45.0	6.23	0.22 ₀	1.79	53.10	90.0	7.38	0.22 ₂	2.82	43.79
"	10.61	0.22 ₂	4.03	42.54	"	11.15	0.26 ₂	—	—
"	20.42	0.24 ₂	3.98	57.61	"	16.23	0.30 ₀	3.18	60.15
"	23.50	0.23 ₂	6.63	51.20	"	21.63	0.33 ₂	—	—
"	25.45	0.24 ₂	6.05	56.15	"	23.76	0.34 ₂	6.40	52.97
"	26.62	0.24 ₂	5.11	59.85	"	24.93	0.35 ₁	—	—
"	29.43	0.25 ₂	8.06	51.97	"	29.72	0.35 ₉	—	—
"	35.03	0.25 ₂	9.74	49.02	"	31.09	0.35 ₀	—	—
"	37.99	0.25 ₇	8.85	53.34	"	31.36	0.34 ₂	—	—
"	43.54	0.24 ₂	10.14	53.66	"	34.16	0.34 ₀	8.76	51.21
*	"	0.20 ₀	48.47	8.69	"	37.24	0.33 ₁	—	—
	49.31	0.20 ₀			"	40.06	0.33 ₂	9.70	50.80
75.0	7.69	0.22 ₂	1.77	65.05	"	43.12	0.32 ₇	9.12	55.15
"	19.60	0.27 ₂	4.83	55.27	"	44.58	0.33 ₀	—	—
"	24.36	0.28 ₇	6.30	54.71	"	46.61	0.32 ₂	13.01	46.54
"	33.32	0.29 ₂	4.61	64.28	"	48.95	0.29 ₁	—	—
"	40.16	0.32 ₁	5.41	62.46	"	49.56	0.29 ₀	12.52	49.58
"	40.88	0.31 ₂	6.11	61.4	"	53.91	0.28 ₀	—	—
"	44.59	0.30 ₂	10.18	51.39	"	57.88	0.26 ₂	12.76	50.54
"	49.70	0.27 ₂	14.29	45.7	"	61.34	0.24 ₂	14.68	48.51
"	58.81	0.24 ₀	12.33	52.40	*	"	72.40	0.18 ₂	45.49
*	"	0.22 ₀	47.47	7.09	*	"	72.54	0.18 ₂	50.98

When the solubility figures are plotted in rectangular co-ordinates, the curves in Fig. 2 are obtained. The maximum on the curves resembles a similar smooth maximum occurring on the solubility temperature curve of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$; it might easily be drawn as a break. When, however, the solubility figures are plotted together with the figures for wet solid phase on a triangular diagram, it appears that $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ is the solid phase throughout. The diagram for 45° is given.

* Both solid phases present in excess.

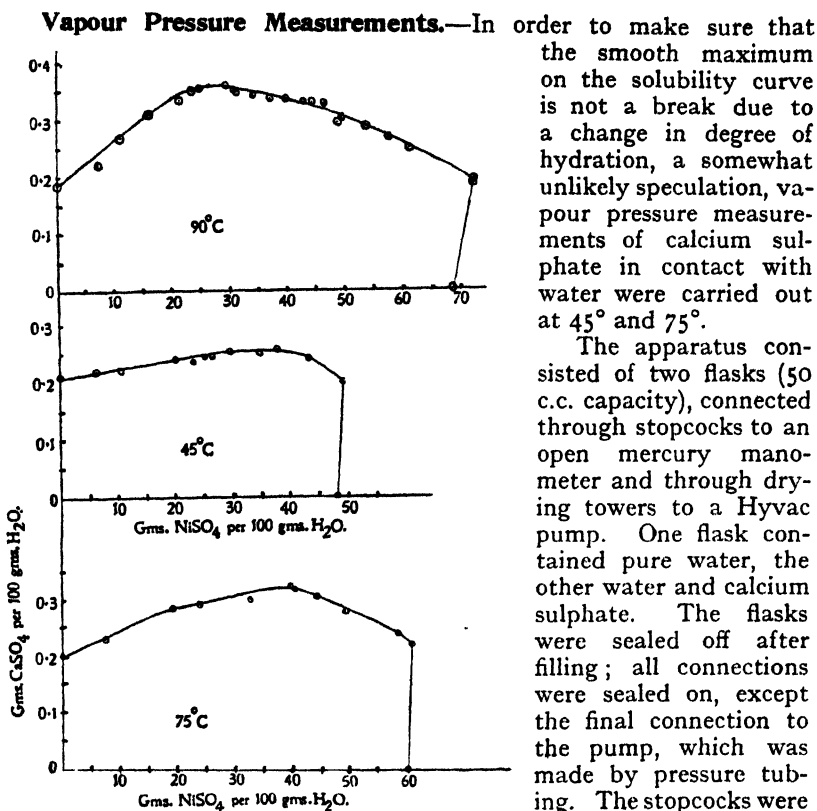


FIG. 2.

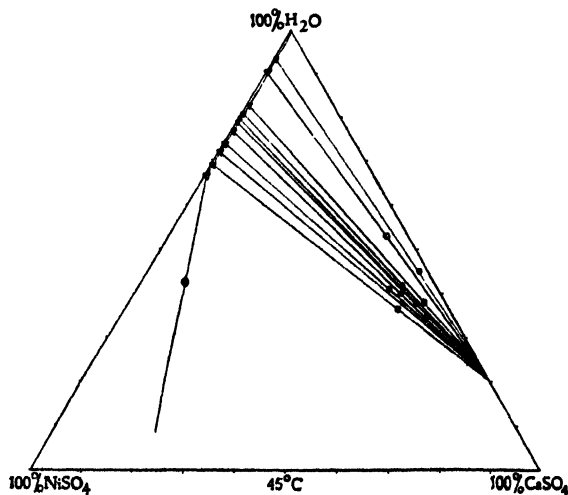


FIG. 3.

the manometer, it was wound with resistance wire connected to the main

The apparatus consisted of two flasks (50 c.c. capacity), connected through stopcocks to an open mercury manometer and through drying towers to a Hyvac pump. One flask contained pure water, the other water and calcium sulphate. The flasks were sealed off after filling; all connections were sealed on, except the final connection to the pump, which was made by pressure tubing. The stopcocks were lubricated with burnt rubber and vaseline, and the apparatus was tested by evacuating and allowing to stand over night. No drop could be detected in the mercury column, which was focussed on the cross-wires of a low power telescope. The apparatus was so constructed that the flasks could be immersed in the thermostat, the manometer projecting into a bottle of mercury on the floor. To prevent condensation of water vapour in

through a rheostat. Any temperature up to red heat could be obtained by varying the rheostat. To prevent cracking of the glass it was protected from the wire by a long column of asbestos paper on all sides except the front. Two thermometers were bound in immediate contact with the glass, by asbestos cord, at suitable heights. The temperature of the manometer was kept 10° above that of the thermostat. The apparatus was evacuated and the bulb containing pure water then put in communication with the manometer, when the mercury fell to a value corresponding roughly to the vapour pressure of water at the temperature in question. The manometer was then evacuated and put into communication with the flask containing calcium sulphate and water, when the mercury fell to exactly the position previously noted. The flask containing gypsum and water was then put into direct connection with the pump and exhausted for a period of from one to five minutes, depending on the temperature of the experiment. The pressure was then read again and so on. At 45° the pressure fell sharply after pumping for some time to a value which remained constant for a further period of pumping, and then fell to zero. At 75° , the drop to zero was immediate, after pumping.

Both series of measurements were repeated with the same result. This corresponds to the result of Van't Hoff and Armstrong* that $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ in contact with natural anhydrite is metastable at that temperature.

Conclusion.

The system $\text{NiSO}_4\text{—CaSO}_4\text{—H}_2\text{O}$, has been studied by the solubility method. Although a maximum occurs on the solubility curve, this is smooth and does not correspond to formation of double salt.

*Department of Chemistry,
University of Manitoba.*

* *Sitzungsber. Akad. Berlin*, 570, 1901 (taken from Mellor's *Treatise of Inorganic Chemistry*; Vol. III, p. 768).

REVIEWS OF BOOKS.

Annual Reports on the Progress of Chemistry. Volume XXVIII for 1931.
(London: The Chemical Society. Price 10s. 6d. Postage, 6d. extra.
Pp. 443.)

The appearance of this well-known report is an event awaited each year with interest by readers of these Transactions. The present volume is of special interest in that two of the Reports will provide useful introductions to forthcoming General Discussions of the Faraday Society; we refer to Dr. Astbury's Report (pp. 322-335) on the Structure of Fibres (September, 1932, General Discussion) and that part of Mr. Bernal and Dr. Wooster's Report which deals with Liquid Crystals (pp. 280-284: April, 1933, General Discussion).

Of the 381 pages devoted to Reports (the remaining pages being devoted to introductory matter and indexes) no less than 168 are given up to matters which are comprised within the scope of these Transactions. The following Reports will therefore prove also of particular interest to Members of the Faraday Society—Dr. Hinshelwood on General and Physical Chemistry (pp. 13-48), Dr. Henry on Electrokinetic Phenomena, Dr. Schofield on the Colloid Chemistry of Clays (pp. 351-366),

Dr. Sidgwick and Dr. Bowen on the Structure of Simple Molecules (pp. 367-403) as well as the remainder of the Report on Crystallography (pp. 262-321).

Members will as usual find that the Reports on Inorganic Chemistry (pp. 49-65), Organic Chemistry (pp. 66-178), Analytical Chemistry (pp. 179-211) and Biochemistry (pp. 212-261) provide a convenient, authoritative and digestible summary of the vast, and less readily assimilable, amount of material which has been published in connection with those branches of the science during the year under review. Incidentally they will be provided with a handy guide to the many points of contact between these subjects and physical chemistry.

Chemistry at the Centenary (1931) Meeting of the British Association for the Advancement of Science. (Cambridge : W. Heffer & Sons, Ltd. Price 7s. 6d. net Pp. xi and 272.)

The occasion of Centenary of the B.A., coinciding with the Faraday Centenary celebrations, brought many distinguished chemists and physicists together in London. Opportunity was taken to arrange groups of memoirs on special subjects, somewhat on the lines of Faraday Society General Discussions though the time occupied in presenting the memoirs prevented any serious general discussion and indeed the memoirs were separate and distinct contributions related only by their common head-subject. The meetings were largely attended and doubtless those present and the many who were unable to be present will welcome the publication of the papers in so convenient and inexpensive a form.

The volume contains the Presidential address of Sir Harold Hartley and the various papers contributed to the discussions on the Influence of the Medium on the Properties of Electrolytes, on Vitamin-A and the Carotenoids, on the Chemistry of Vitamin-B and related Problems (which included Vitamin-D), on the Structure of Simple Molecules, as well as to the Symposium on the British Fuel Problem. Reports are also given of the few *ad hoc* contributions to the various discussions.

A Text-book of Organic Chemistry. By Professor Dr. JULIUS SCHMIDT. Second English Edition. By Dr. H. GORDON RULE. (London : Gurney & Jackson. Pages xxiv and 843. Price 25s. net.)

We have here an admirable text-book of the "Honours" type. A prefatory General Section deals with such matters as Molecular Structure and Isomerism. Part I. (pp. 98-346) is devoted to the Aliphatic compounds, Part II. (pp. 347-561) to the Carbocyclic compounds and Part III. (pp. 562-793) to the Heterocyclic compounds. The remainder of the volume is devoted to a full author and subject index.

The book is admirably produced and strongly bound. In addition to its more obvious use by Honours students it should make a strong appeal to those (such as physical chemists) who want a not too voluminous book of reference or reminder in a subject with which they come into only occasional contact.

Perkin and Kipping's Organic Chemistry. By F. STANLEY KIPPING and F. BARRY KIPPING. (London : W. & R. Chambers, Ltd. Pages—Part I., xi and 323 ; Part II., vi and 290, with General Index, xxix. Price 8s. 6d.)

Most chemists were brought up on an early dose of Perkin and Kipping. A new edition is always, therefore, regarded with interest. The volume has been brought up-to-date whilst retaining the original plan. The whole of the work has been reset so as to give the authors free scope. The two parts are bound in one volume and cover very much the lines to which we are accustomed. A Part III. adapted for Honours Students is to follow.

Stainless Iron and Steel. By J. H. G. MONYPENNY, F.Inst.P. Second Edition. (London, 1931: Chapman & Hall, Ltd. Pp. ix + 575 with 55 plates. Price 25s.)

The appearance of this greatly enlarged and improved edition will be welcomed by metallurgists and by many others who have felt the inconvenience of the book being out of print for more than three years. The first edition (1926) was fully reviewed in these *Transactions* (Vol. XXIII., 1927, pp. 266-8). The delay in the publication of the second edition has enabled the author to include a large amount of recent work. It is to all intents and purposes a new book, the original matter having been rearranged and largely re-written and new matter added to the extent of doubling the length of the book. It is lavishly illustrated with photomicrographs, and diagrams are constantly used throughout, with great advantage, for expressing numerical data.

After an extended historical survey, successive chapters deal with the influence of chromium on the structure and hardness of steel, the mechanical and physical properties of high chromium steels, the influence of other alloys on the properties of high chromium steels, the effect of varying treatment and composition on the resistance to corrosion of stainless steels, the resistance to various types of corroding media, heat-resisting steels, manufacture, working and treatment, and the selection of steels for industrial purposes.

Stainless steels and the closely allied heat-resisting steels are now an important group of engineering materials, and their use is steadily extending. Their resistance to corrosion is mainly due to their chromium content, 10 to 25 per cent. or even more, and chromium is still the only essential alloy element in the simpler types. By additions of nickel (sometimes in large amount), silicon, copper, cobalt, molybdenum or tungsten, together with selection of carbon content and of heat treatment the properties of the steel may be greatly modified. Thus, different steels are produced which by their varied mechanical properties combined with resistance to oxidation are fitted to withstand many types of severe corrosive conditions under which ordinary steels would rapidly fail. The considerably higher cost of these special steels may be many times repaid by their longer life. In the chemical trade stainless steel vessels may have the additional merit of not contaminating their contents.

Recognising the scientific study of the iron-chromium-carbon system, within a certain range of composition, as the basis of a sound knowledge of the stainless steels, the author gives a good account of what is known of this system and of the influence of chromium on the structure and properties of steel. Recent developments in the use of very high chromium contents, 25 per cent. or more, by which increased resistance to certain types of corrosion may be secured, account for the inclusion of much new matter, dealing with this part of the system. Of special interest is the section on the effect of chromium in extending the range of existence of α -iron and reducing that of γ -iron, an effect having practical drawbacks sometimes necessitating measures to counteract it.

Of the other alloy elements added to stainless chromium steels nickel is by far the most important, and the valuable group of austenitic stainless steels, including "Staybrite," "Anka" and "V2A," owe their properties mainly to the effect of 25 per cent. or more of nickel and chromium together. The author gives an excellent account of these steels and the more complex steels of which they are the basis. The precipitation of

carbides when austenitic stainless steels are heated in the range 500° - 900° C. or are slowly cooled through this range, the consequent embrittlement under corrosive conditions and the remedies, such as the addition of titanium and tungsten, applied to prevent this troublesome "weld-decay" are clearly explained. The remarkable properties of the "ATV" group of high nickel high chromium steels are fully described.

As a small selection of the many subjects on which important fresh information is given may be mentioned the effect of cold-work on austenitic and other types of stainless steel used for deep-drawing operations, the free-cutting stainless steels, temper-brittleness and its control, fatigue and corrosion-fatigue, "creep" at raised temperatures in the heat-resisting steels, and the welding of stainless steels.

As the term "stainless steels" is now universally applied to a great variety of steels differing widely in composition, the retention of the term "stainless iron" for one simple low-carbon variety seems unnecessary; it might well be omitted from both the title and the text of future editions.

Constant use of the first edition has shown that the praise bestowed on it in our review was well deserved. The second edition is far better still. Through his intimate association with the development of stainless steels and his position in the industry the author has qualifications for writing on this subject which few can equal, and the book bears evidence on almost every page of the care and thoroughness with which he has discharged his task.

H. M.

Die Quantenstatistik und ihre Anwendung auf die Elektronentheorie der Metalle. Von LÉON BRILLOUIN. (Berlin: Julius Springer, 1931. Pp. x + 530. Price 42 R.M., gebunden 43.80 R.M.).

This book is undoubtedly one of the most interesting and instructive which have been written on quantum statistics and the electron theory of metals. It is based on two volumes bearing a similar title published in French by the author in 1930, but radical changes and additions have been made in the German edition, chiefly in reference to the theory of metals.

The book begins with an account of the theory of radiation and the enunciation of the Planck law. Then there is a concise but very clear statement of the methods of wave mechanics with a number of applications to which reference is made in the later parts of the book. This is followed by an account of statistical mechanics and quantum statistics.

The two main chapters of the book (amounting to over 200 pages) deal with the application of Fermi statistics to the free electrons in metals and the wave-mechanical methods developed by Bloch, Peierls and others, to build up a satisfactory theory of the electrical and thermal properties of metals. This account of recent theories, including as it does new considerations due to the author, is undoubtedly one of the most comprehensive and most critical which has yet been published.

As far as possible the author has aimed at making his book a complete and self-consistent whole. It is well written, is illustrated by many instructive diagrams and is admirably printed. No student of the theory of metals should be without it, and no reader will close the book without a clearer idea of quantum mechanics and quantum statistics.

THE DIRECT TITRATION OF NITRATES WITH TITANOUS CHLORIDE USING ALIZARIN AS AN ADSORPTION INDICATOR.

BY A. W. WELLINGS.

Received 6th June, 1932.

The work recorded in this paper resulted from attempts to discover a simple reduction method for the direct titration of nitrates in aqueous solution. In the first place, no expectation of the possibility of employing an adsorption indicator was entertained, on account of the difficulty of obtaining a precipitate in the titration process, owing to the distinct solubility of nitrates in general. When, however, titanous chloride was employed as the reducing agent, it was found, under certain conditions, that a precipitate of $\text{Ti}(\text{OH})_3$, or, possibly, TiO_2 , was formed by the hydrolysis of titanous chloride. The use of an adsorption indicator was thus rendered possible.

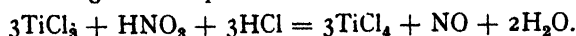
Preliminary Investigations.—The starting point of the investigation was the belief that titanous chloride in hydrochloric acid solution should be oxidised to titanic chloride by solutions of nitrates.

As a preliminary, a standard solution of sodium nitrate was acidified with hydrochloric acid, boiled, and titrated with standard titanous chloride, in the hope that the persistence of the blue colour of the titanous chloride would give a satisfactory "end-point". Although there was no doubt, from the appearance of the reacting solutions with some evolution of nitrous fumes, that the titanous chloride had been oxidised, a satisfactory "end-point" was not observed.

Various substances were then tried as indicators, and, eventually, it was found that alizarin gave a deep green solution with acidified titanous chloride, and a yellow solution with acidified titanic chloride.

Aliquot portions of 0.1 molar solutions of various nitrates were acidified with concentrated hydrochloric acid, raised to boiling-point, and titrated with standard titanous chloride, using a few drops of a one per cent. alcoholic solution of alizarin as the indicator. The mixture was kept at the boiling point throughout the titration.

In some cases fairly satisfactory "end-points" were obtained, but in many cases the colour change from light yellow to green passed through intermediate shades of colour, and a sharp "end-point" could not be obtained. From the general results obtained, however, it was clear that *one* molecule of nitric acid had oxidised *three* molecules of titanous chloride, probably according to the equation



For example, it was found that 25 mls. of a 0.1 molar solution of the nitrate of a univalent metal, and 25 mls. of a 0.05 molar solution of the nitrate of a bivalent metal, were equivalent to between 70 and 80 mls. of 0.1 molar titanous chloride.

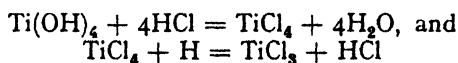
The Conditions under which a Precipitate is Formed during the Titration.—In order to ascertain if the "end-point" of the titration could be made more distinct, the method of titration was varied.

25 mls. of 0.1 molar sodium nitrate were *not acidified, but diluted to 100 mls. with distilled water* (it was believed that the colour change, yellow to green, might be more distinct in diluter solutions, and in the absence of excess acid). The addition of a small amount of alizarin solution produced a red coloration. The mixture was then boiled and titrated with the standard titanous chloride.

The addition of the first few drops of titanous chloride produced a deep greyish-green colloidal solution, the colour of which disappeared on boiling, the original red colour being restored. As the titration proceeded a precipitate was formed, and it was observed that the colour change occurred on the particles of the precipitate. The titration was continued until the red colour was no longer restored on boiling, the "end-point" being denoted by the permanent grey colour of the mixture. The result was quantitative.

Identification of the Precipitate.—From the comparatively large amount of precipitate formed, it seemed very unlikely that it was derived from the alizarin (only 3 mls. of 1 per cent. alizarin solution were employed). A more probable explanation was that the titanous chloride formed in the titration had been hydrolysed by the boiling water to titanous hydroxide, and, possibly, partly converted to titanium dioxide.

In order to test this hypothesis, the precipitate was filtered, washed with alcohol to remove any alizarin, and dissolved in boiling concentrated hydrochloric acid. Metallic zinc was then added, and when the reduction of the solution was completed, a violet-blue solution of titanous chloride remained. The precipitate was, therefore, either Ti(OH)_4 or TiO_2 , and the reactions can be expressed by the equations



The Quantitative Estimation of Nitrates.—Estimations were carried out on decinormal solutions of the nitrates of Na, K, NH_4 , Pb, Mg, Cd, Co, Ca, Ba, Mn, Sr, Cu, UO_2 , and Al, using a standard TiCl_3 solution about 0.14 molar. With the exception of uranyl nitrate, the results were quantitative within the limits of experimental error. The case of uranyl nitrate was exceptional in that no precipitate of Ti(OH)_4 was formed in the titration. This may have been due to the fact that the uranyl radical had converted it to either titanium uranate or diuranate. The "end-point" of the titration had to be determined by the colour change of the solution from red through yellow (due to HCl) to green, and was, therefore, less accurate. Negative results were obtained in the case of silver nitrate, since the large precipitate of silver chloride formed during titration obscured the colour change, and there also seemed to be some reduction to silver or silver oxide. No attempts were made to estimate the nitrates of bismuth and mercury as these salts form insoluble basic nitrates. All the nitrates used in the determinations were either guaranteed analytical reagents, or were prepared in the laboratory, recrystallised, and carefully dried. In any case where the number of molecules of water of crystallisation was in doubt, it was determined gravimetrically.

Experimental Details and Precautions.

A. The Concentrations of the Reactants.—If the nitrate solution is approximately decinormal (with reference to HNO_3), the portions

to be titrated must be diluted considerably in order to assist the hydrolysis of the TiCl_4 . Nitrates may be estimated in centinormal solution, provided that adequate volumes are titrated; for example, 50 mls. of a centinormal nitrate solution will be equivalent to 15 mls. of 0.1 molar titanous chloride. On the other hand, since a good yield of titanic hydroxide is essential, it is inadvisable to employ solutions of titanous chloride in concentrations weaker than 0.1 molar.

B. The Standardisation of, and Method of Titrating with, Titanous Chloride.—Owing to the ease with which titanous chloride can be oxidised to titanic chloride by atmospheric oxygen, the standardisation, and subsequent titrations, must be carried out in an atmosphere of hydrogen. The method of standardisation is that employed for the standardisation of titanous chloride for the estimation of ferric salts, full details of which are given in any text-book of Volumetric Analysis. The apparatus employed is that usually employed for a titanous chloride titration; a burette being connected to a reservoir containing the titanous chloride in an atmosphere of hydrogen.

The solutions of titanous chloride used by the author were prepared as follows: 200 mls. of commercial 15 per cent. titanous chloride solution were mixed with 400 mls. of concentrated hydrochloric acid, and diluted to 1 litre with air-free distilled water. On standardisation this yielded a solution about 0.14 molar.

C. The Indicator Solution.—A 1 per cent. solution of alizarin in alcohol was employed, about 3 mls. being taken in each titration.

D. Precautions to be Observed in the Titration.—

(i) Sufficient water must be present to ensure efficient hydrolysis of the titanic chloride to the hydroxide.

(ii) The nitrate solutions must be raised to boiling-point before titration, and must also be boiled after each addition of titanous chloride. The author found that in some cases one or two minutes boiling were necessary to restore the red colour of the solution of nitrate with alizarin at the commencement of the titration; as the titration proceeded, however, only a few seconds boiling were necessary until the "end-point" was reached.

Summary.

Nitrates may be estimated rapidly and accurately in decinormal and centinormal solutions by titration with standard titanous chloride. Alizarin is used as an adsorption indicator, the colour change occurring on the particles of titanic hydroxide formed by hydrolysis, on boiling, during the titration.

Leamington College.

SOLUBILITIES OF THE PHOSPHATES OF LEAD.*

BY MAURICE JOWETT AND HAROLD IDRIS PRICE.

Received 7th June, 1932.

This investigation was begun with the object of redetermining the solubilities of tertiary lead phosphate, $\text{Pb}_3(\text{PO}_4)_2$, and of secondary lead phosphate, PbHPO_4 , in aqueous solutions.

Millet and Jowett¹ had previously measured the solubilities of these salts. The consistency of the measurements, and the constancy of the solubility products calculated, led to the belief that the results were valid. The lead electrode was used, however, in presence of oxygen, and further investigation has shown that the results of Millet and Jowett are inaccurate.

The present work shows that in the presence of chloride ion both tertiary and secondary lead phosphate are transformed to pyromorphite, $\text{Pb}_5(\text{PO}_4)_3\text{Cl}$. The formation of this salt is of interest from a geological point of view, and also throws some light on the reactions of lead compounds in the blood stream.

We have determined the solubility products of the three salts in aqueous solutions at 37.5°C ., and calculated their ranges of stability. The measurements were made in part in dilute solutions, and as regards pyromorphite in solutions of ionic strength $0.16M$.

The fluid lead amalgam electrode and the quinhydrone electrode have been used in this work.

Technique of Lead Electrode Measurements.

Some measurements at 25°C ., for standardising purposes, were made in the same way as those of Millet.²

The method used by Millet for removing oxygen from the solutions by bubbling nitrogen through them is on theoretical grounds inefficient.

We have preferred for our other measurements to use a box-like rocking electrode vessel (Fig. 1) of similar shape to, and rocked in the same manner as, the manometric vessels of Warburg.³ The vessel has three exits in its flat top, which is just covered by the thermostat liquid. The middle exit allows nitrogen to pass out. The other two are fitted with rubber bungs. Through one of them liquid connection is made to a beaker containing saturated KCl solution, in which also dips a normal calomel electrode vessel. Through the other enters nitrogen (previously

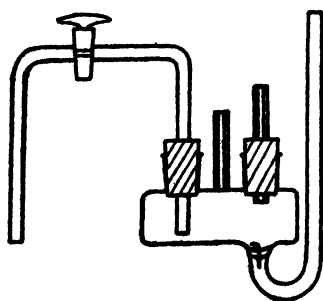


FIG. 1.

* This investigation was undertaken on behalf of the Liverpool Medical Research Organisation. (Director: Professor W. Blair Bell.)

¹ Millet and Jowett, *J. Amer. Chem. Soc.*, **51**, 997, 1929.

² Millet, *Trans. Faraday Soc.*, **25**, 147, 1929.

³ Warburg, *Über den Stoffwechsel der Tumoren*, 4, 108, Berlin, 1926.

passed over heated copper and washed), and subsequently the lead amalgam, from an amalgam holder like those of Millet.² When amalgam enters it settles in a hollow and makes contact with a platinum wire sealed through the glass and leading to an external connection.

The vessel has a capacity of about 20 c.c., and requires 8-10 c.c. of solution for a measurement. The solution is rocked in the electrode vessel for about twenty minutes while nitrogen is passing through, and amalgam is then run in. Equilibrium is rapidly attained between gas and liquid, and so oxygen is rapidly removed from the solution.*

The lead amalgams used were of various strengths, and were standardised by measuring the E.M.F. values they gave in the cells at 37.5° C. when in contact with a solution of $M/1000$ lead chloride in $0.157M$ sodium chloride. $0.01M$ HCl sometimes replaced an equivalent amount of NaCl in this solution; the E.M.F. was not altered by this change. The activity of lead ion in the standardising solution is taken, as explained later, as $10^{-3.956}$, this being the basis for calculating lead-ion activities from other measurements. Standardisation was frequently repeated, although the normal calomel electrodes were usually constant for several months at 37.5° C.

Measurements with the standard solution were usually exactly reproducible; with other solutions variations seldom exceeded 0.3 mv. The E.M.F. values did not vary with time; a steady value is reached within five minutes and maintained for several hours.

We have not succeeded in making satisfactory measurements in the presence of nitric acid.

Chemical Determination of Lead and Phosphate.

In dealing with solutions containing nitric acid, we have determined lead by titration of lead chromate. The method is well-known, but some of the details given are important for its accurate use.

The solution to be estimated, containing preferably several mgms. of lead, is acidified with HCl, gassed with H_2S , adjusted with caustic soda to be acid to phenolphthalein, and allowed to stand overnight, after being made up accurately to 25 c.c. The lead sulphide precipitate is filtered—a measured volume of the filtrate is boiled and employed for phosphate determination—and dissolved completely in hot nitric acid. The acid solution is neutralised with caustic soda and slightly acidified. Potassium chromate is added and the solution is brought to boiling-point and allowed to stand overnight. The lead chromate precipitate is washed on the centrifuge, dissolved in dilute HCl, and the chromic acid titrated with sodium thiosulphate solution (about $N/300$) after addition of potassium iodide. Blank titrations are made, and the thiosulphate is freshly standardised with a potassium chromate solution. The method is accurate to 1 per cent. if 2 mgms. of lead or more are taken, as was usually done.

Phosphate determinations were made according to the colorimetric method of Briggs,⁴ as employed by Jowett and Lawson,⁵ which gives results accurate to about 1 per cent. when carefully used, the mean of several determinations being taken.

* With the manometric vessels of Warburg under these conditions equilibrium is reached between a gas phase and liquid to 1 per cent. in about three minutes.

⁴ Briggs, *J. Biol. Chem.*, **59**, 255, 1924.

⁵ Jowett and Lawson, *Biochem. J.*, **25**, 1981, 1931.

Standardisation of Lead Electrode Measurements.

Our problem is to obtain a value of $\gamma_{Pb^{2+}}$ at 37.5° C. for solutions approximating to 0.16M NaCl, and also to calculate values of $\gamma_{Pb^{2+}}$ for a number of dilute solutions not containing halide ions.

According to the data of Carmody⁶ the activity coefficients of lead chloride diverge considerably even in dilute solution from the values given by the simple Debye equation. Scatchard and Tefft⁷ suggested that this might be due to partial association of Pb^{2+} to $PbCl^+$, and the idea has been confirmed by Fromherz and Lih⁸ by means of spectroscopic measurements, from which have been obtained approximate estimates of the extent of the association. Fromherz⁹ has hence calculated that the corrected values of the activity coefficients of lead chloride follow the Debye equation in dilute solutions, when use is made of the value 0.1267 v. for the E_0 of the lead electrode at 25° C.

The value 0.1267 v. may therefore be taken at present as the best, although Fromherz favours a higher value.* Carmody and others have obtained 0.0058 v. for the E.M.F. between metallic lead and a saturated lead amalgam at 25° C.; we have confirmed this value. Accordingly E_0 for a saturated amalgam is 0.1209 v., and this value can be applied to calculate the E.M.F. of the cell:—

Pb	PbX ₂		N	Hg
saturated	($a_{Pb^{2+}} = m$)	Saturated	KCl	
amalgam		KCl		Hg ₂ Cl ₂

We use the value -0.2812 v. for the normal calomel, since this corresponds, according to Randall and Young,¹⁰ to the value of the silver-silver-chloride electrode used by Carmody. If liquid-junction potentials cancel out, the E.M.F. of the cell is given by the relation:

$$E = 0.4021 - 0.02956 \log m.$$

Liquid-junction potentials may not, however, cancel out, and some measurements made by us at 25° C. will therefore be used to calculate the constant to be employed in the formula. The amalgams used by us were not saturated, and the E.M.F. values (E) as given in Table I. are corrected to the values that a saturated amalgam would show. The cells were otherwise as illustrated above.

TABLE I.— $PbCl_2$ — $NaCl$ SOLUTIONS AT 25° C.

Solution.	μ	E .	E_0' .	$E_0' - 0.05911 \sqrt{\mu}$.
0.001 M $PbCl_2$, 0.160 M NaCl .	0.163	0.5205	0.4318	0.4079
0.001 M $PbCl_2$, 0.087 M NaCl .	.09	.5143	.4256	.4079
0.001 M $PbCl_2$, 0.037 M NaCl .	.04	.5080	.4193	.4075
0.001 M $PbCl_2$, 0.007 M NaCl .	.01	.5007	.4120	.4061

$$(E_0' = E - 0.02956 \log C_{Pb^{2+}}).$$

⁶ Carmody, *J. Amer. Chem. Soc.*, **51**, 2905, 1929.

⁷ Scatchard and Tefft, *J. Amer. Chem. Soc.*, **52**, 2272, 1930.

⁸ Fromherz and Lih, *Z. physik. Chem.*, **153A**, 321, 1931.

⁹ Fromherz, *ibid.*, 376.

* Fromherz proposes the value 0.1274 v., although the value 0.2812 v. for the normal calomel would lead instead to 0.1284 v.

¹⁰ Randall and Young, *J. Amer. Chem. Soc.*, **50**, 989, 1928.

The values in the last column of Table I. cannot be extrapolated satisfactorily to infinite dilution, since the slope of the curve increases in the more dilute solutions when we plot against $\sqrt{\mu}$. An approximate evaluation of E_0 for the cell can, however, be made with the help of Carmody's data on lead chloride solutions. Taking E_0 for the lead electrode to be 0.1267 v., and assuming that γ_{Cl^-} obeys the simple Debye equation, we have hence calculated, in Table II., values of $\gamma_{Pb^{2+}}$ for lead chloride solutions. Corrected values for $\gamma_{Pb^{2+}}$ have also been derived, allowance being made for the association of lead ion according to Fromherz. In the last two columns of Table II. are values of $\gamma_{Pb^{2+}}$ calculated from our measurements of Table I., E_0 for our cells being taken as 0.4033 v. This value has been chosen to make the two sets of values for $\gamma_{Pb^{2+}}$, corrected according to Fromherz, agree for the two most dilute solutions.

TABLE II.—VALUES OF $\gamma_{Pb^{2+}}$

$\sqrt{\mu}$	PbCl ₂ Solutions.		PbCl ₂ — NaCl Solutions.	
	$\gamma_{Pb^{2+}}$	$\gamma_{Pb^{2+}}$ (Corr.).	$\gamma_{Pb^{2+}}$	$\gamma_{Pb^{2+}}$ (Corr.).
0.1	0.524	.562	0.508	0.561
0.2	.286	.358	.288	.406
0.3	.180	.270	.176	.333
0.404	—	—	.1086	.276

In employing the value 0.4033 v. for strong solutions we are regarding the liquid-liquid P.D. as independent of the composition of the lead-containing solution. As the value 0.4033 v. is close to the value 0.4021 v. previously calculated, which may itself be too low, liquid-liquid P.D.'s are probably not of great magnitude.

From the uncorrected values of $\gamma_{Pb^{2+}}$, we interpolate a value 0.111 for $\gamma_{Pb^{2+}}$ in sodium chloride solutions of ionic strength 0.16M at 25° C. The temperature coefficient of this value depends on the unknown temperature coefficient for the association of lead ion, and we have merely to assume therefore that the same value holds good at 37.5° C.*

We have also to find a basis for calculating lead-ion activity coefficients at 37.5° C. for various dilute solutions which do not contain halide ions, and in which therefore the lead is probably all present as lead ion. We assume the validity of the Debye equation :

$$-\log \gamma_{Pb^{2+}} = 0.515n^2\sqrt{\mu},$$

which fits in adequately with our data.

Measurements with the Quinhydrone Electrode.

The quinhydrone electrode has been used, at 37.5° C., to determine hydrogen-ion activities. Gold electrodes have been chiefly used, in electrode vessels of 5-10 c.c. capacity. The quinhydrone is washed in the electrode vessel with a portion of the solution, which is then renewed. A saturated KCl solution connects the half-element with a normal calomel electrode.

* On this assumption the cell constant, which is 0.4033 v. at 25° C., becomes 0.4020 v. at 37.5° C., this value being derived from measurements at both temperatures on a cell containing the standard lead solution.

We have found it troublesome to make the accurate and reproducible measurements that were desired, as the electrodes often change their values after a few measurements. We have accordingly standardised all measurements on the basis that 0.01*N* HCl in 0.09*N* KCl gives an E.M.F. of 0.2820 v., this being the best value found. Electrodes were tested every few measurements with the standardising solution: steady and reproducible measurements were often found anywhere within the range 0.2816 to 0.2821 v. An electrode showing the value 0.2816 v., for example, was taken to give E.M.F.'s 0.0004 v. too low. Duplication of corrected values was frequently exact, and divergences seldom exceeded 0.3 mv. Unsatisfactory measurements could usually be detected by a slow downward drift of the E.M.F. with time: in a good measurement the value was steady in the period between ten and twenty-five minutes after setting up the cell. No reliable means was found of restoring electrodes to correct behaviour: they usually returned to normal values on standing in water. The coarse gold deposit obtained by plating electrodes in acid solutions of gold chloride gives very good values, but the deposits wear off rapidly.

For calculating hydrogen-ion activities (p_H values) we have taken γ_H in the mixture 0.01*N* HCl + 0.09*N* KCl to be 0.84, this being one basis mentioned by Clark.¹¹ To interpret our measurements, we assume (1) that the liquid-junction potentials in our cells are the same as in the case of the standard HCl—KCl solution, and (2) that the E_0 of the quinhydrone electrode is independent of the solution. The second assumption is little in error for our solutions¹²; the first is the easier alternative to making doubtful calculations of liquid-junction potentials. That such calculations are far from finality may be seen from the work of Bjerrum and Unmack,¹³ according to whom, moreover, the corrections

TABLE III.—QUINHYDRONE ELECTRODE MEASUREMENTS.*

Solution.	E.	— log γ_H .
0.01 <i>N</i> HCl, 0.09 <i>N</i> KCl	0.2820	(0.076)
0.01 <i>N</i> HCl2818	.080
0.03 <i>N</i> HCl3112	.080
0.1 <i>N</i> HCl3425	.094
0.01 <i>N</i> HCl, 0.15 <i>N</i> NaCl2829	.062
0.015 <i>N</i> HCl, 0.135 <i>N</i> NaCl,2937	.062
0.02 <i>N</i> HCl, 0.14 <i>N</i> NaCl3010	.068
0.04 <i>N</i> HCl, 0.12 <i>N</i> NaCl3196	.068
0.01 <i>N</i> HNO ₃2822	.073
0.017 <i>N</i> HNO ₃2961	.078
0.03 <i>N</i> HNO ₃3111	.081

¹¹ Clark, *The Determination of Hydrogen Ions*, 3rd edition, 1928.

¹² See references given by Clark (*l.c.*), and by Jowett and Millet, *J. Amer. Chem. Soc.*, 51, 1004, 1929.

¹³ Bjerrum and Unmack, *Det. Kgl. Danske Videnskabernes. Selskab. Mathematisk-fysiske Meddelelser.*, IX., 1, 1929.

* Our results are in agreement with those of others. Bjerrum and Unmack,¹³ using the hydrogen electrode, a 3.5 *N* KCl boundary, and a decinormal calomel, found at 37° C. the E.M.F. values 0.4624, 0.4022 for cells containing respectively 0.01 *N* HCl + 0.09 *N* KCl, and 0.1 *N* HCl. Correcting to 37.5° C., their values are 0.4626, 0.4023. Taking the E.M.F. between the decinormal and normal calomel to be 0.0551 according to Bjerrum and Unmack, and the E.M.F. between the hydrogen and quinhydrone electrodes to be 0.6897 according to Biilmann and Krarup (*J. Chem. Soc.*, 125, 1954, 1924), we calculate that the E.M.F. of our quinhydrone cells containing these solutions should be 0.2822, 0.3425.

to be applied are frequently not more than 0.5 mv. Our measurements are interpreted by the equation

$$0.0616 p_{\text{H}^+} = 0.4099 - E,$$

where E is the corrected E.M.F. of the cell containing the (acid) solution.

Some measurements made on various solutions are given in Table III. The values of γ_{H^+} are only to be interpreted formally: they are useful for comparing our standardisation of p_{H^+} values with those of others, and as showing the likely extent to which liquid-junction potentials enter.

The Ionisation Constants of Phosphoric Acid.

As our measurements have been made in acid solutions, the second and third ionisation constants of phosphoric acid enter our calculations only as additive constants. When we have determined the equilibrium in our solutions between $\text{H}_2\text{PO}_4'$ and H_3PO_4 , defined according to the relations:

$$p_{K_1} = p_{\text{H}^+} + p_{\text{H}_2\text{PO}_4'} - p_{\text{H}_3\text{PO}_4},^*$$

$$p_{K_1'} = p_{\text{H}^+} + p_{\text{H}_2\text{PO}_4'} - p_{\text{H}_3\text{PO}_4},^\dagger$$

we find the activities of HPO_4'' and PO_4''' by the relations:

$$p_{K_2} = p_{\text{H}^+} + p_{\text{HPO}_4''} - p_{\text{H}_2\text{PO}_4'},$$

$$p_{K_3} = p_{\text{H}^+} + p_{\text{PO}_4'''} - p_{\text{HPO}_4''}.$$

The values of p_{K_2} and p_{K_3} at 37.5° C. have been taken to be 7.165 and 12.18, according to Bjerrum and Unmack. The $p_{a_{\text{H}^+}}$ of 0.01*N* HCl + 0.09*N* KCl is, according to these authors, 2.055, while we have taken the p_{H^+} of this solution as 2.076; the difference in standardisation has not been corrected for.

Values of $p_{K_1'}$ at 37.5° C. have been determined (a) in dilute solutions, and (b) in solutions of ionic strength 0.16*M*, by measuring the p_{H^+} of solutions made up from mixtures of potassium dihydrogen phosphate and hydrochloric acid. The data are given in Table IV.

TABLE IV.

KH_2PO_4	HCl	NaCl	p_{H^+}	μ	$p_{K_1'}$	p_{K_1}
0.010	0.010	—	2.295	0.0160	2.126	2.191
0.015	0.005	—	2.764	0.0170	2.158	(2.225)
0.01667	0.010	—	2.417	0.0212	2.109	2.184
0.018	0.011	—	2.384	0.0229	2.099	2.177
0.025	0.009	—	2.604	0.0279	2.111	2.197
0.025	0.011	—	2.495	0.0288	2.105	2.192
0.03	0.008	0.1276	2.659	0.1601	2.007	—
0.03	0.012	0.1262	2.450	0.1602	2.004	—
0.03	0.0176	0.1239	2.243	0.1605	2.006	—

In the dilute solutions the value 0.070 has been assigned to $-\log \gamma_{\text{H}^+}$, in the strong solutions 0.062. Values of the hydrogen-ion concentration are calculated from the p_{H^+} values, and used to determine the amount

* These terms are negative logarithms of the activities or activity constant.

† The terms in this equation (except p_{H^+}) relate to concentrations.

of hydrogen ion that has disappeared in converting H_2PO_4' into H_3PO_4 . The values of p_{K_1}' can hence be derived. We assume that in dilute solutions

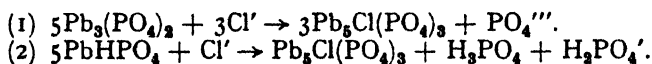
$$p_{K_1} = p_{K_1}' + 0.515 \sqrt{\mu} = p_{K_1}' - \log \gamma_{H_2PO_4}'$$

and derive a value 2.188 for p_{K_1} at 37.5° C. The value found by Bjerrum and Unmack at 37° C. is 2.232; either value may be in error by 0.02, as the correct values to use for γ_{H^+} are in doubt. Our value for p_{K_1} is the better for our purposes, when used with our assumed value of γ_{H^+} .

For solutions of ionic strength 0.16M we find that p_{K_1}' has the value 2.006. We hence assume that in these solutions $-\log \gamma_{H_2PO_4}'$ has the value 0.182.

Pyromorphite.

We have now to consider the evidence for the formation of pyromorphite from the secondary and tertiary phosphates of lead in the presence of chloride ion, and also the solubility of this salt. The equations for the formation are:



The direct evidence that we have for reaction (1) is of a qualitative nature, and consists in the fact that when solid $Pb_3(PO_4)_2$ is left in slightly acid chloride solutions, soluble phosphate appears in solution, and the p_{H^+} rises, as we have found many times. Indirect evidence will be given later.

Equation (2) has been tested in a more quantitative manner.

1.821 gms. of $PbHPO_4$ were shaken at 37.5° C. for several days with 100 c.c. of a solution containing 0.094M HCl and 0.048M NaCl.

The p_{H^+} changes showed that reaction was probably complete in a few hours.

The phosphate and chloride concentrations were estimated after a few days. They, together with the p_{H^+} measurements, lead to the following results:—

	Obs.	Calc.
Change in chloride concentration . . .	— 0.0124	— 0.0120
„ phosphate concentration . . .	+ 0.0252	+ 0.0240
„ hydrogen-ion concentration . . .	— 0.011	— 0.011

The observed changes agree satisfactorily with those calculated on the basis of equation (2). To the actual observed changes have been applied small corrections for the calculated solubility of pyromorphite. We will not enter into these, or the calculation of the hydrogen-ion changes, in order to save space. Repetition gave similar results.

While the phosphorus content of the $PbHPO_4$ was found to be 10.46, 10.21 per cent. (theoretical 10.24), that of the presumed pyromorphite was 6.83, 7.15, 7.08, 7.18 per cent.* (theoretical: $Pb_5Cl(PO_4)_3$ 6.87, $Pb_3(PO_4)_2$ 7.65).

Measurements of the solubility of pyromorphite will now be considered. Solid $PbHPO_4$ or $Pb_3(PO_4)_2$, or both, made in a manner similar to that

* Some of the solids analysed were from the solubility determinations considered later.

of Millet and Jowett,¹ were added to 100 c.c. of solution,* of ionic strength about 0.16*M*. The mixtures were rotated in 100 c.c. bottles in a thermostat at 37.5° C. for about a month, samples being withdrawn for estimation over the periods 5 to 32 days. Measurements of $p_{\text{Pb}^{2+}}$ (the negative logarithm of the lead-ion activity) and of $p_{\text{H}^{+}}$ were made electrometrically on the solutions, and phosphate was estimated in the filtrates. Lead was also estimated chemically in a few of the solutions; the results agreed with the electrometric values within a few per cent. None of the measured quantities showed regular changes with time, and the values in Table V. are mean ones.

We expected to measure the solubilities of PbHPO_4 and $\text{Pb}_3(\text{PO}_4)_2$, either singly or in equilibrium, but examination of the data obtained showed that neither of these salts could be in equilibrium with the solutions. In the case of PbHPO_4 it was also visible to the eye that the salt had changed to another substance. If $p_{\text{Pb}^{2+}}$ is plotted against $p_{\text{PO}_4^{3-}}$, a single straight line is obtained of the type

$$p_{\text{Pb}^{2+}} + k p_{\text{PO}_4^{3-}} = \text{const.},$$

where k is very near to 0.60. The theoretical value for $\text{Pb}_3(\text{PO}_4)_2$ is 0.667. Now, as only small quantities of solid were added to the solution, little chloride will have disappeared if the salts have changed to pyromorphite. The solubility product relation for pyromorphite we will write as:

$$5p_{\text{Pb}^{2+}} + 3p_{\text{PO}_4^{3-}} + p_{\text{Cl}^{-}} = p_{\text{S}_6}$$

From this relation, if the chloride-ion concentration is constant, we would expect to find $k = 0.60$ in the former equation. The view that pyromorphite is formed is thus substantiated by the solubility data. These data alone could not prove it: they are in as good agreement with the idea that the solid phase is $\text{Pb}_3(\text{PO}_4)_2 \cdot \text{HCl}$. We have therefore obtained some evidence that such a compound is not formed: when the still-wet solid phase is boiled with caustic soda solution, no acid is released, as would probably happen with such a compound.

We turn to a consideration of Table V. The original chloride concentrations were from 0.156 to 0.160*M*. As the weights of solids taken were unknown, the decreases in the chloride concentrations that have occurred (taking formation of pyromorphite as established) were calculated from the changes in the $p_{\text{H}^{+}}$ and in the phosphate concentrations, using equations (1) and (2) and related equations. Details will not be given of the calculations: the corrected values range only from 0.151 to 0.158*M*. The values of $p_{\text{H}_2\text{PO}_4^{+}}$ and $p_{\text{PO}_4^{3-}}$ are calculated by means of the data already given. The term P is the total phosphate concentration.

In calculating p_{S_6} , the solubility-product term, the term used for the chloride ion is a concentration term, though it would be more logical to assume a value for $\gamma_{\text{Cl}^{-}}$ and employ an activity term.

It will be seen that the constancy of p_{S_6} is satisfactory: a mean value of 79.115 is derived.

In the calculations the ionic strength is taken as 0.16—the actual values ranged from 0.1548 to 0.1602, averaging 0.1586.

* $\text{Pb}_3(\text{PO}_4)_2 + \text{PbHPO}_4$ in Nos. 1-8; $\text{Pb}_3(\text{PO}_4)_2$, Nos. 9-11; PbHPO_4 , Nos. 12-14. HCl and NaCl only were present initially in Nos. 1-8 (HCl up to 0.04*M*). In the others KH_2PO_4 was initially present, up to 0.01*M*. NaCl made up the bulk of the electrolyte.

TABLE V.—SOLUBILITY OF PYROMORPHITE.

No.	$p_{Pb^{++}}$	p_{H^+}	P.	$p_{H_2PO_4'}$	$p_{PO_4^{'''}}$	p_{S_2}
5	3·828	1·516	0·00216	3·459	19·772	79·263
1	4·085	1·549	·00477	3·091	19·338	79·255
9	4·111	1·742	·00200	3·334	19·195	78·940
6	4·172	1·771	·00208	3·298	19·101	78·967
12	4·177	1·531	·00805	2·877	19·160	79·168
3	4·210	1·664	·00366	3·123	19·140	79·279
10	4·445	1·950	·00211	3·187	18·632	78·922
13	4·477	1·716	·00877	2·709	18·622	79·055
7	4·491	1·960	·00200	3·206	18·631	79·149
4	4·497	1·813	·00449	2·938	18·657	79·264
0	4·594	1·947	·00287	2·997	18·448	79·114
11	4·754	2·140	·00237	3·046	18·111	78·903
14	4·774	1·928	·01050	2·503	17·992	(78·655)
8	4·842	2·206	·00209	3·074	18·007	79·032
2	4·962	2·000	·00869	2·547	17·892	79·306
						79·115

Some measurements made with pyromorphite under conditions of lower solubility may be briefly mentioned. The measurements were made with the electrode vessels of Millet,² and are indicated in Table VI.

The E.M.F. values rose with time, after the well-washed solid was introduced, but appeared to reach limiting values. The fact that the values observed for $p_{Pb^{++}}$ are lower than those calculated from the solubility product of pyromorphite just deduced, is probably due to the electrode dissolving in presence of some residual oxygen, the effect being noticeable at low lead-ion concentrations. Nevertheless there is qualitative support for the view that pyromorphite is the stable salt under these conditions.

TABLE VI.—PYROMORPHITE IN ACETATE BUFFER SOLUTIONS.

($\mu = 0.16$, $C_{Cl^-} = \text{approx. } 0.14 M.$)

p_{H^+}	P.	$p_{Pb^{++}}$ (obs.).	$p_{Pb^{++}}$ (calc.).
3·995	0·010	7·30	7·52
4·576	0·001	7·47	7·61
5·089	0·001	8·15	8·23

Secondary Lead Phosphate.

The solubilities of secondary lead phosphate, $PbHPO_4$, were measured in dilute nitric acid solutions at 37·5° C. 0·5 gm. of the solid was added in each case to 100 c.c. of nitric acid solution, and the bottle was rotated for two days (Nos. 40-43) or seven days (Nos. 27-29) in the bath before sampling. Lead and phosphate estimations were made on the solutions by the chemical methods already described. The quinhydrone E.M.F.'s showed a drift in some cases, and there was therefore reason to believe that the electrode was not functioning accurately in the solutions.* This was confirmed by two facts: (1) the solubility

* The electrodes showed steady values in HCl—KCl solutions, and gold quinhydrone electrodes are evidently sometimes sensitive to oxidising properties of HNO_3 solutions.

products obtained using the observed p_{H^+} values did not show very good constancy, and (2) the observed p_{H^+} values did not lead to good balancing of the equation

$$2C_{Pb^{++}} + C_{H^+} = C_{H_2PO_4'} + C_{HNO_3'}$$

We have therefore preferred to calculate values of p_{H^+} from this equation, and to use the calculated values for obtaining the solubility product. The values are calculated from those of C_{H^+} by assuming $-\log \gamma_{H^+}$ equal to 0.075.*

The data and calculations are shown in Table VII. Values of p_{H^+} and μ are obtained by successive approximations. Values of $C_{H_2PO_4'}$ are obtained from the equation

$$p_{K_1'} = 2.188 - 0.515\sqrt{\mu} = p_{H^+} - \log \frac{C_{H_2PO_4'}}{C_{H_3PO_4}}$$

with the use of the observed values for total phosphate (P). From $C_{H_3PO_4}$ is calculated $p_{H_3PO_4'}$, assuming $-\log \gamma_{H_3PO_4'}$ equal to $0.515\sqrt{\mu}$. We then derive $p_{HPO_4''}$ from the equation for $p_{K_2'}$ given already. We next calculate $p_{Pb^{++}}$ from $p_{C_{Pb^{++}}}$ assuming, as already indicated, that $\gamma_{Pb^{++}}$ follows the Debye relation.

The value of p_{S_2} is finally derived from the equation

$$p_{S_2} = p_{Pb^{++}} + p_{HPO_4''}$$

The mean value derived for p_{S_2} is 11.36. In all the solutions the total phosphate concentration is higher than that of lead, showing that the solid $PbHPO_4$ is contaminated with some soluble phosphate.

TABLE VII.—SOLUBILITIES OF $PbHPO_4$ IN NITRIC ACID SOLUTIONS.

No.	Initial Concn. of HNO_3	$C_{Pb^{++}}$	P.	p_{H^+} (obs.).	p_{H^+} (calc.).
40	0.00800	0.000995	0.001200	2.310	2.250
27	0.00983	0.001141	0.001388	2.246	2.158
41	0.01300	0.001619	0.001723	2.032	2.052
28	0.01671	0.001832	0.002172	1.998	1.932
42	0.02100	0.002611	0.002746	1.846	1.851
29	0.02948	0.003426	0.003700	1.716	1.700
43	0.03500	0.004059	0.004476	1.622	1.627

No.	$\sqrt{\mu}$	$C_{H_2PO_4'}$	$p_{HPO_4''}$	$p_{Pb^{++}}$	p_{S_2}
40	0.0985	0.000678	8.136	3.205	11.341
27	0.108	0.000715	8.210	3.165	11.375
41	0.124	0.000790	8.280	3.046	11.326
28	0.1395	0.000859	8.372	3.024	11.396
42	0.157	0.000980	8.405	2.906	11.311
29	0.1845	0.001066	8.532	2.845	11.377
43	0.2005	0.001157	8.578	2.805	11.383
				Mean	11.358

* Very similar values of C_{H^+} are derived by calculation from the initial concentration of nitric acid and the acid neutralised in converting the $PbHPO_4$ going into solution into H_2PO_4' and H_3PO_4 .

Tertiary Lead Phosphate.

As will be shown later, tertiary lead phosphate is stable only under conditions where its solubility is very small. The measurements recorded below have been made under conditions where the salt is unstable, and transformation to secondary lead phosphate is usually proceeding.

To 100 c.c. of a dilute solution of lactic acid, in which a little sodium nitrate was present to give sufficient conductivity for p_H measurements, was added 0.5 gm. of $Pb_3(PO_4)_2$, and the solutions were sampled several times at fairly short intervals; after filtration p_H measurements, and lead and phosphate estimations were made. The solid was a fine powder, and the solutions had sometimes to be filtered twice, by which time their temperatures had fallen several degrees.

If transformation to $PbHPO_4$ is not proceeding, the lead concentration should be about 50 per cent. greater than the phosphorus concentration; this is the case in No. 45. In Nos. 44 and 46 transformation is occurring according to the equation:

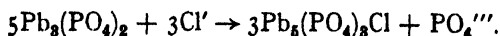
TABLE VIII.—SOLUBILITY OF $Pb_3(PO_4)_2$.

No.	Initial Concn. of Lactic Acid.	Concn. of $NaNO_3$	Time of Sampling (mins.).	$C_{Pb^{++}}$	P.	p_H	$\sqrt{\mu}$	$p_{Pb^{++}}$	$p_{PO_4^{'''}}$	p_{S_p}
44 (a)	0.08	0.01	50	0.002246	0.000865	2.595	0.1405	2.938	17.414	43.642
(b)			100	0.003052	0.000607	2.640	.148	2.820	17.471	43.402
(c)			150	0.003347	0.000369	2.709	.150	2.784	17.536	43.424
46 (a)	0.04	0.01	40	0.001404	?	2.682				
(b)			80	0.001555	0.000773	2.724	.130	3.076	17.172	43.572
(c)			120	0.001967	0.000476	2.797	.1335	2.981	17.225	43.393
45 (a)	0.02	0.01	100	0.000896	0.000630	2.907	.119	3.293	16.859	43.597
(b)			150	0.000887	0.000620	2.899	.119	3.297	16.883	43.657
47	0.04	0.01 *	40	0.00093	0.000222	2.639	.114	4.266	17.897	(48.592)

* NaCl is present in this case instead of $NaNO_3$.

The phosphorus concentration decreases as time passes, and the p_H rises.

In the case of No. 47, 0.01M NaCl replaces $NaNO_3$, and the data show that transformation to pyromorphite is taking place. The phosphate concentration has become, in forty minutes, greater than that of lead, as it should according to the equation



The calculation of the solubility product of $Pb_3(PO_4)_2$, given by the equation

$$p_{S_p} = 3p_{Pb^{++}} + 2p_{PO_4^{'''}}$$

has been made by the methods already described. The data from bottles 44-46 give a roughly constant value for p_{S_p} : the fact that No. 45 gives the same value as the others, although in this case only is the

tertiary phosphate the only solid phase, shows that the transformation taking place to PbHPO_4 has not yet prevented saturation of the solutions with $\text{Pb}_3(\text{PO}_4)_2$. The mean value of p_S , derived is 43.53.

No. 47 gives a much lower value for the ionic product of $\text{Pb}_3(\text{PO}_4)_2$. The calculated value for the ionic product of pyromorphite is 77.0, the chloride concentration being taken as unchanged; the value is rapidly approaching the saturation value of 79.1. In this case the solution is undersaturated with respect to PbHPO_4 , in the other cases the solutions are supersaturated with respect to it, as of course they should be; these conclusions have been drawn using the solubility product for PbHPO_4 already determined.

Determinations of the equilibrium between PbHPO_4 and $\text{Pb}_3(\text{PO}_4)_2$ may, of course, be made, but experiments made with a view to this showed that even in fairly acid solutions, where the equilibrium should be set up most rapidly, equilibrium is not reached in a fortnight, and the phosphate concentrations are inconveniently low for measurement. In less acid solutions, where the phosphate concentration at equilibrium could be measured conveniently, some months would probably be required for equilibrium to be attained.

Equilibria between the Three Salts.

The values for the solubility products for the three salts are assembled in Table IX, in which it is shown that the average deviation from the mean, taking into account the number of ions concerned, is about the same.

TABLE IX.

Salt.	p_S .	Deviation.	n .	Deviation/ n .
PbHPO_4 . .	11.36	± 0.028	2	± 0.014
$\text{Pb}_3(\text{PO}_4)_2$. .	43.53	± 0.109	5	± 0.022
$\text{Pb}_3\text{Cl}(\text{PO}_4)_2$. .	79.115	± 0.125	9	± 0.014

The equilibrium between PbHPO_4 and $\text{Pb}_3(\text{PO}_4)_2$ can be defined by the relation

$$C_{\text{H}_3\text{PO}_4} = \frac{K_3^2 S_2^3}{K_1 K_2 S_3},$$

and our data lead to the conclusion that at equilibrium the concentration of H_3PO_4 is about $2.8 \cdot 10^{-6} M$.^{*} If the concentration of H_3PO_4 has a higher value, PbHPO_4 only will be stable, and vice versa. That is, PbHPO_4 is usually the stable salt in more acid solutions, $\text{Pb}_3(\text{PO}_4)_2$ in less acid solutions.

Equilibrium between PbHPO_4 and pyromorphite will exist when the relation satisfied is

$$\frac{a_{\text{H}^+} \times a_{\text{HPO}_4}''}{C_{\text{Cl}^-}} = \frac{S_2^5 \cdot K_3^3}{S_3 \cdot K_2^2} = 1.3.$$

^{*} In experiments approaching the equilibrium from the acid side, a value as low as $6 \cdot 10^{-8} M$ was observed, equilibrium being not yet attained.

Hence, if the chloride-ion concentration is appreciable, PbHPO_4 can only exist at equilibrium when the acidity and phosphate concentration are high.

Equilibrium between pyromorphite and $\text{Pb}_3(\text{PO}_4)_2$ is expressed by the equation :

$$\frac{a_{\text{PO}_4'''}}{C_{\text{Cl}'}} = \frac{S_3^5}{S_5^3} = 10^{19.7}.$$

Evidently if the chloride-ion concentration * is as high as $1 \cdot 10^{-6} M$, this value is sufficiently high to prevent $\text{Pb}_3(\text{PO}_4)_2$ from having a stable existence except under very extreme conditions.

Discussion.

Previous work need only be reviewed briefly. The measurements at Harvard¹⁴ on the solubilities of PbHPO_4 and $\text{Pb}_3(\text{PO}_4)_2$ in lactic acid solutions do not allow of solubility-product calculations. The data of Millet and Jowett,¹ when compared with the present data, afford evidence that the lead electrode was not functioning correctly in presence of oxygen, although the work of Millet² had suggested that the conditions were satisfactory. In the experiments of Maxwell and Bischoff¹⁵ on the solubility of $\text{Pb}_3(\text{PO}_4)_2$ in salt solutions pyromorphite was probably formed, and this will perhaps explain the results that puzzled these authors.

The fact that pyromorphite is the stable salt in aqueous solutions containing a little chloride, probably explains why compounds of the pyromorphite type occur in nature in preference to PbHPO_4 or $\text{Pb}_3(\text{PO}_4)_2$.

PbHPO_4 does not appear to occur in nature, and $\text{Pb}_3(\text{PO}_4)_2$ only in one mineral, ferrazite, in which lead is partly replaced by barium. On the other hand, pyromorphite, $\text{Pb}_5\text{Cl}(\text{PO}_4)_3$ or $\text{PbCl}_2 \cdot 3\text{Pb}_3(\text{PO}_4)_2$, is a main constituent of many minerals, in which calcium and other metals may partly replace lead, and vanadate and other acid groups may partly replace phosphate.

Of the lead compounds of which we have measured the solubilities, pyromorphite will be the most stable in the body. Evidence has, however, been obtained that the compound formed in the blood when soluble lead salts are added to it contains calcium, as well as lead and phosphate. On the ground that stability in the body may parallel stability in the earth, we could argue that the compound likely to be formed would be of the pyromorphite type, with calcium replacing some lead. The matter will be more fully discussed in a forthcoming paper.

Summary.

1. The solubilities in aqueous solutions at 37.5°C . of secondary lead phosphate (PbHPO_4), tertiary lead phosphate ($\text{Pb}_3(\text{PO}_4)_2$), and pyromorphite ($\text{Pb}_5\text{Cl}(\text{PO}_4)_3$) have been determined, and solubility products calculated.

* We are neglecting for chloride ion the difference between activity and concentration.

¹⁴ Aub, Fairhall, Minot, Reznikoff, *Medicine Monographs*, **7**, 35, 1926.

¹⁵ Maxwell and Bischoff, *J. Pharm. Exp. Therap.*, **36**, 279, 1929.

2. In presence of even very low chloride-ion concentrations, pyromorphite is the stable salt. Secondary and tertiary lead phosphates are in equilibrium at a phosphoric acid concentration of about $3 \cdot 10^{-6}$ M.

3. A value for the E_0 of cells containing a lead electrode and a liquid junction (saturated KCl) has been obtained. A rocking electrode vessel for use with fluid lead amalgams is described.

4. The quinhydrone electrode is used with an accuracy of about 0.1 mv. The first ionisation constant of phosphoric acid at 37.5° C. has been determined.

*Muspratt Laboratory of Physical and Electro-Chemistry,
University of Liverpool.*

THE PROPAGATION OF EXPLOSION WAVES THROUGH A SYSTEM OF GLASS AND RUBBER TUBES.

BY COLIN CAMPBELL, ALFRED KING AND CLIFFORD WHITWORTH.

Received 20th June, 1932.

The velocity of a detonation wave along a tube of constant diameter was found by Berthelot¹ to be independent of the nature of the material of the tube, identical results being obtained with tubes of metal and of rubber. Dixon² observed that if two tubes forming part of a gallery were jointed together by means of a connection such as rubber, which could yield to the shock, the velocity of the explosion was diminished at the junction; if the junction was rigid no change in velocity was observed. Audibert³ photographed the explosion as it passed from one glass tube through an opaque rubber tube and into a second glass tube. He concluded that, with electrolytic gas ($2\text{H}_2 + \text{O}_2$), the explosion passed through the rubber tube without change of velocity; if, however, the mixtures $2\text{H}_2 + \text{O}_2 + \text{N}_2$ and $\text{CH}_4 + 2\text{O}_2$ were used, the velocities in the two glass tubes were equal but greater than the velocity in the rubber tube. In these experiments the glass and rubber tubes all had internal diameters of 12 mm. and the lengths were between 60 and 80 cm. No details are given as to the mode of ignition of the mixtures, the thickness of the rubber, and whether the rubber burst or remained intact.

Laffitte,⁴ in repeating these experiments, was unable to find any marked fall in flame velocity in the rubber tube. Any *small* change in velocity he attributed to a small abrupt increase in the diameter of the gallery where the rubber tube fitted over the glass tube. In view of the apparent lack of agreement between the observations of Audibert and Laffitte the following experiments have been carried out.

Experimental.

The explosion gallery consisted of lead, glass and rubber tubes all of 1.5 cm. internal diameter, joined together as shown in Fig. 1. The

¹ *Ann. Chim. Physique* (V.), 28.

² *Compt. rend.*, 178, 1275, 1924.

³ *Phil. Trans.*, 200A, 305, 1903.

⁴ *Ann. Physique* (10), 4, 636, 1925.

glass tubes had a wall thickness of 0.2 cm. in all cases, but rubber tubing of the following thicknesses was employed in different experiments; 0.45 cm., 0.3 cm., 0.2 cm., 0.1 cm. and 0.025 cm. When the thinnest tube, made out of Excelsior Rubber Dam, was used it was not possible to get a joint which would hold a vacuum, and the system was filled, therefore, by sweeping through a large quantity of the gas mixture; in all other cases the tubes were evacuated by means of an oil pump and filled with the undried mixture at about 17° C. The rubber tubes were slipped over the glass tubes to the extent of a few centimetres and wired on.

Preliminary experiments showed that the same results were obtained whether the mixture was lit by a taper flame at the open end of the gallery or by an electric spark when this end was closed, provided that in each case detonation was set up in the mixture some distance from the rubber. In all the following experiments spark ignition near the closed end of the tube was employed, the further end being open. With those mixtures which require a long "run" before the establishment of the explosion wave when fired by a spark, a little $2\text{H}_2 + \text{O}_2$ or $\text{C}_2\text{H}_4 + 3\text{O}_2$ mixture was introduced at the firing end just prior to ignition, so that the explosion wave might be fully established before the flame entered the rubber. The gallery was placed horizontally in front of a drum camera rotating at speeds between 15 and 60 m.p.s., and records were obtained of the flame movement in the glass tubes and also in the rubber tube, where

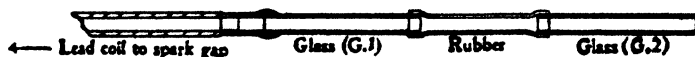


FIG. 1.

this was translucent. Where the velocities of the flames in the first glass tube were constant and equal to the accepted velocities of the fully-established explosion waves in the different mixtures, it was assumed that a steady condition had been established and that the different experiments were strictly comparable.

The mixtures employed were of hydrogen, carbon monoxide, methane, ethylene and acetylene respectively with differing amounts of oxygen; in certain cases nitrogen and carbon dioxide were added. With regard to the behaviour of the explosion waves in these experiments the mixtures seem to fall into two fairly well defined classes, as will be seen below.

Class 1.—In mixtures belonging to this class the explosion wave shows no appreciable change in velocity as it passes along the gallery, quite irrespective of the length or thickness of the rubber section and whether the rubber bursts or remains intact; in different experiments the rubber varied in length between 3.5 cm. and 100 cm. and in thickness between 0.025 cm. and 0.2 cm. The mixtures used by M. Audibert fall into this class and will be discussed first.

A photograph, obtained with the mixture $2\text{H}_2 + \text{O}_2$, is reproduced in Fig. 2. Examination of the trace due to the flame front showed that the explosion wave passed through the glass and rubber tubes at a constant velocity of about 2800 m.p.s. The small arrows in the figure indicate points corresponding with the ends of the rubber tube which was 20.5 cm. long and 0.025 cm. thick. It may be seen that the rubber burst soon after the flame front had passed. The mixtures $2\text{H}_2 + \text{O}_2 + \text{N}_2$ and $\text{CH}_4 + 2\text{O}_2$, under the same conditions, gave records similar to those obtained with $2\text{H}_2 + \text{O}_2$, indicating a constant velocity throughout the

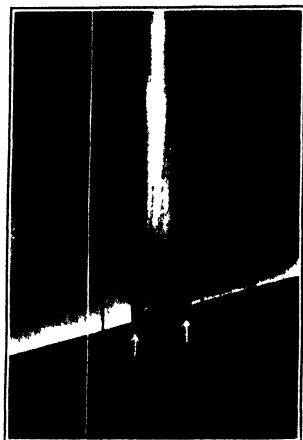


FIG. 2. Explosion in $2\text{H}_2 + \text{O}_2$. Flame unretarded by passage through rubber tube (0.025 cm. thick).

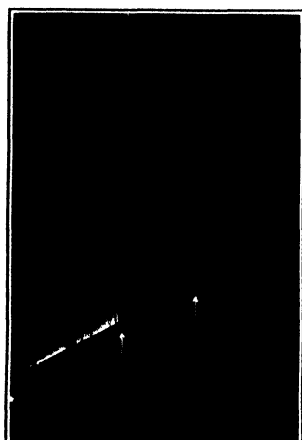


FIG. 3. Explosion in $\text{C}_2\text{H}_4 + 4\text{O}_2 + 4\text{CO}_2 + \text{N}_2$. Flame retarded after passing through rubber tube (0.1 cm. thick).



FIG. 4. Explosion in $2\text{CO} + \text{O}_2$. Flame retarded in rubber tube (0.025 cm. thick).



FIG. 6. Explosion in $2\text{H}_2 + \text{O}_2 + \text{SO}_2$. Flame slightly retarded after passing through rubber tube.

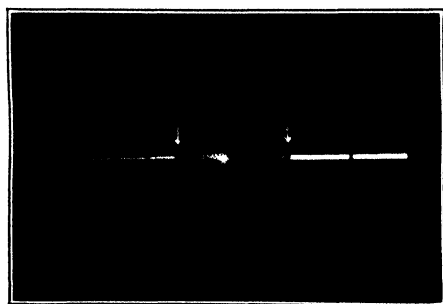


FIG. 5.—Record on stationary plate: mixture $2\text{CO} + \text{O}_2 + 1$ per cent. H_2 . Note narrow central band in rubber section.

system. Thus, while the record of flame movement in $2\text{H}_2 + \text{O}_2$ agreed with the result obtained by M. Audibert, his observations concerning the other mixtures are not confirmed.

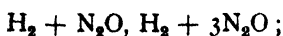
It was thought desirable to make observations with a series of combustible gas-oxygen mixtures of increasing dilution under similar conditions to those above. Since dilution of electrolytic gas with either oxygen or hydrogen resulted in mixtures giving explosion waves of such feeble actinic quality that measurable flame traces could not be obtained, a series of acetylene-oxygen mixtures was investigated although the reactions occurring were probably more complex. Mixtures varying in composition between $\text{C}_2\text{H}_2 + 3\text{O}_2$ and $\text{C}_2\text{H}_2 + 17\text{O}_2$ when sparked in the lead tube all gave fully established explosion waves moving at constant velocity in the first glass tube. In no case was there any appreciable fall in flame velocity in the rubber tube. The velocities of the flames in the two glass tubes are given in Table I.

TABLE I.

Mixture.	Velocities (m p.s.) in	
	G ₁	G ₂
$\text{C}_2\text{H}_2 + 3\text{O}_2$. . .	2310	2320
$\text{C}_2\text{H}_2 + 5\text{O}_2$. . .	2090	2080
$\text{C}_2\text{H}_2 + 7\text{O}_2$. . .	1970	1965
$\text{C}_2\text{H}_2 + 9\text{O}_2$. . .	1900	1865
$\text{C}_2\text{H}_2 + 11\text{O}_2$. . .	1820	1785
$\text{C}_2\text{H}_2 + 13\text{O}_2$. . .	1760	1720
$\text{C}_2\text{H}_2 + 15\text{O}_2$. . .	1690	1690
$\text{C}_2\text{H}_2 + 17\text{O}_2$. . .	1645	1640

The maximum difference between the velocities in the two tubes is about 40 m.p.s., rather less than 3 per cent. of the velocity of the flame in the mixture concerned ($\text{C}_2\text{H}_2 + 13\text{O}_2$). This difference, though small and approaching the limit in accuracy of measurement of the photographs, does appear to be real since the flame traces were side by side on the same record, which fact enables small velocity differences to be detected even if not accurately measured. It may, however, be said that with mixtures of this series there is little or no appreciable fall in velocity -- the characteristic property of mixtures in Class 1. (In passing it should be noted that in these experiments the propagation of an explosion wave has been observed in a number of mixtures containing less than 10 per cent. C_2H_2 , the previously recorded limit for propagation.⁵ A further mixture containing 5 per cent. C_2H_2 , which propagated an explosion wave with a velocity of 1610 m p.s., will be included in Class 2.)

Similar records, showing little or no appreciable fall in velocity, were also obtained with the following mixtures:—



Methane-Oxygen mixtures with methane content between 50 per cent. and 18.3 per cent;

Ethylene-Oxygen mixtures with ethylene content between 40.5 per cent. and 8.6 per cent.

⁵ Le Chatelier, *Ann. de Chim. et Physique*, 20, 15, 1900; *Comptes. rend.*, 130, 1755, 1900.

The records obtained with the mixtures quoted above were, in general, seen to be alike in one other respect, *viz.*, they did not show well defined and regular striæ such as have been observed in records of explosion waves in carbon monoxide-oxygen and other mixtures.* Ill-defined and/or irregular striæ were observed only in a very few cases, *e.g.*, $C_2H_2 + 17O_2$. Thus it would appear to be general that in mixtures which do not exhibit well-defined striæ in the photographs, the explosion wave is able to pass through the system without appreciable change in velocity.

It was known that certain explosive mixtures on addition of sufficient carbon dioxide gave mixtures which exhibited well-defined striæ; these come under Class 2 and will be discussed there. Mixtures such as $2H_2 + O_2 + \frac{1}{2}CO_2$, $2H_2 + O_2 + \frac{1}{2}CO_2$, $C_2H_4 + 3O_2 + CO_2$, and $C_2H_4 + 3O_2 + 2\frac{1}{2}CO_2$, containing insufficient carbon dioxide to produce well-defined striæ in the photographs, showed no appreciable change in explosion wave velocity.

Class 2.—In these mixtures the explosion waves can be made to suffer a change in velocity when they pass through the rubber tube, if suitable conditions are chosen. Whether or not this happens appears to depend, with different mixtures, on such factors as the length and thickness of the rubber and whether it bursts or remains intact. In general, the flame has a lower velocity on entering the second glass tube (G_2) than it had in the first glass tube (G_1). Fig. 3 shows a typical case of a fall in velocity in the second glass tube. The mixture with which this record was obtained was $C_2H_4 + 3O_2 + 4CO_2 + N_2$. The rubber tube, though a little thicker than that used in the experiment corresponding with Fig. 2, was again burst, and it will be seen that the luminosity in the second glass tube was very much less than in the first. In a few cases the flame showed a fall in velocity while still passing through the rubber section, and in Fig. 4 is reproduced a record of flame movement of this type, obtained with the mixture $2CO + O_2$ when a rubber tube of length 20.5 cm. and thickness 0.025 cm. was employed. The reproduction shows little trace due to the flame after entering the second glass tube, but examination of the original record showed that it had actually traversed the whole length of this tube with an average velocity of 90 m.p.s. (In some records there was a more or less luminous wave sent back from the beginning of the rubber tube, probably caused by the slight irregularity at the glass-rubber joint.)

The following mixtures belong to Class 2 and they are probably typical of many others. It is to be noted that the photographs of the explosion waves in these mixtures all show very well-defined striæ.

- (a) $2H_2 + O_2 + CO_2$; $2H_2 + O_2 + SO_2$.
- (b) Methane-Oxygen mixtures containing either excess methane, *e.g.*, 53 per cent. CH_4 , or diminished methane content, *e.g.*, 15.3 per cent., 14.5 per cent. and 13.3 per cent. CH_4 .
- (c) Ethylene-Oxygen mixtures containing excess ethylene, *e.g.*, 62.3 per cent. C_2H_4 , or diminished ethylene content, *e.g.*, 7.3 per cent., 6.3 per cent., 4.8 per cent., C_2H_4 .
- (d) $C_2H_4 + 3O_2 + 3CO_2$; $C_2H_4 + 3O_2 + 4CO_2$; $C_2H_4 + 3O_2 + 4CO_2 + N_2$.

* Campbell and Woodhead, *J.C.S.*, 1572, 1927; Bone and Fraser, *Proc. Roy. Soc.*, 130A, 542, 1931.

(e) $2\text{CO} + \text{O}_2$ alone or containing small quantities of hydrogen. On increasing the amount of hydrogen the striæ are no longer evident and the mixtures then fall into Class 1.

(f) $\text{CO} + \text{N}_2\text{O}$.

(g) $\text{C}_2\text{H}_2 + 19\text{O}_2$.

The following examples will serve to show how the different experimental conditions affect the behaviour of the mixtures in Class 2.

The Effect of Thickness of Rubber.

It is evident that if the rubber be of sufficient thickness it will approximate to a rigid tube and should then have no effect on the velocity of the wave. As the thickness diminishes the rubber will expand more easily and might, therefore, be expected to have a greater effect on the velocity of the explosion wave; this has been shown to be the case.

A typical example is given in Table II.

TABLE II.

Mixture.	Rubber.		Velocity (m.p.s.)		
	Length.	Thickness.	in G_1 .	in G_2 .	in Rubber.
53 % CH_4 in O_2	30 cm.	0.45 cm.	2300	2300	2300
53 % CH_4 in O_2	30 cm.	0.30 cm.	2300	Too faint to measure	Falling

Thus, no fall is obtained when a thick rubber tube was used, but a fall resulted with thinner rubber.

The Effect of Bursting of the Rubber.

It seems probable that if the rubber bursts it will be more likely to produce a fall in the velocity of an explosion wave than if it remains intact, and an example of this is given in Table III. In this Table is also recorded the result of slitting with a razor blade a very short length of thick rubber just prior to firing the mixture; the rubber thus becomes a "Bunsen Valve."

TABLE III.

Mixture.	Rubber.			Velocity (m.p.s.)		
	Length.	Thickness.	Final Condition.	in G_1 .	in G_2 .	in Rubber.
$2\text{H}_2 + \text{O}_2 + \text{CO}_2$	10 cm.	0.1 cm.	Burst	1800	'Slow'	Falling
$2\text{H}_2 + \text{O}_2 + \text{CO}_2$	10 "	0.1 "	Intact	1830	1800	1800
$2\text{CO} + \text{O}_2$	30 "	0.3 "	Slit	1750	800	Falling
$2\text{CO} + \text{O}_2$	30 "	0.3 "	Intact	1750	1750	1750

Effect of Length of Rubber.

In general the less the length of rubber, other conditions being constant, the less is the tendency of the explosion wave, in any particular mixture, to fall in velocity. This is shown for two mixtures in Table IV.

TABLE IV.

Mixture.	Rubber.		Velocity (m.p.s.)		
	Length.	Final Condition.	in G ₁ .	in G ₂ .	in Rubber.
2H ₂ + O ₂ + CO ₂	20 cm.	Intact	1930	'Slow'	—
2H ₂ + O ₂ + CO ₂	15 "	Intact	1930	1960 *	1930
2H ₂ + O ₂ + CO ₂	10 "	Burst	1930	1930	1930
6.3 % C ₂ H ₄ in O ₂	42 "	Burst	1580	'Slow'	Falling
6.3 % C ₂ H ₄ in O ₂	21 "	Burst	1630	1660	1630

With the first mixture in the above table no appreciable fall occurred with tubes 15 or 10 cm. long, although in the latter case the tube burst; with a 20 cm. tube a fall occurred in the rubber and in the second glass tube. In the case of the ethylene mixture the tube burst in both cases but a fall only occurred with the longer tube. (In the case of the velocity marked with an asterisk there was a small fall in G₂ with a rapid recovery to detonation.)

Effect of Change of Composition of Mixture.

With the mixtures in Class 2 it has been found that a small change in the composition of the mixture often caused the flame to show alteration in velocity under any given conditions of rubber tube. Thus, using mixtures made by adding small quantities of hydrogen to 2CO + O₂ the following results were obtained with a rubber tube 0.025 cm. thick and 15 cm. long.

TABLE V.

Mixture.	Behaviour of Flame Speed		Stria.
	in Rubber.	in G ₂ .	
2CO + O ₂	Falling	Extremely slow flame	Well defined
2CO + O ₂ + (1 % H ₂)	Falling	Very slow flame	Well defined
2CO + O ₂ + (2 % H ₂)	No fall	Slow flame	Fairly definite
2CO + O ₂ + (3 % H ₂)	No fall	Slow flame only after travelling some 30 cm.	Faintly visible
2CO + O ₂ + (7 % H ₂)	No fall	No fall	Absent

Thus the addition of 7 per cent. or more of hydrogen prevented a fall in the second glass tube even with the thinnest rubber. In other experiments where thicker rubber was used (0.01 cm. thick) the addition of 1.5 per cent. H₂ was sufficient to prevent a fall.

The behaviour of the mixtures 2CO + O₂ + (2 per cent. H₂) and 2CO + O₂ + (3 per cent. H₂) must be considered in more detail. It is to be noted that the flame front passed through the rubber tube at normal explosion rate, but that a fall in velocity occurred in the second glass tube. Many other examples of this phenomenon have been observed in the course of this investigation. It seems evident, therefore, that expansion of the rubber tube after the flame front has passed through

has a marked influence on the velocity of the flame further ahead. As evidence that the rubber did not respond immediately to the pressure exerted by the flame, we may quote experiments in which photographs were taken on stationary films. In one experiment of this type, the mixture used was $2\text{CO} + \text{O}_2 + (1 \text{ per cent. } \text{H}_2)$ and the rubber tube was 30 cm. long and 0.1 cm. thick.

The photograph (Fig. 5) shows a fairly well-defined continuous narrow band of light corresponding with the undisturbed position and normal size of the rubber; round this is a less luminous and wider portion showing the flame in the expanded rubber. Since the rubber was burst by the explosion and was not in position after the experiment, the narrow band of light must have been due to flame in the tube before expansion took place and the flame front therefore must have passed any point in the rubber before expansion occurred there.

These results make improbable any explanation based on instantaneous reduction of pressure in the wave-front, and suggest that release of pressure behind the wave-front is responsible for the retardations observed. During the time taken by the rubber to respond to the pressure exerted, the flame front has been travelling at normal explosion rate. If the rubber is not too long, this time may be such that the flame front has reached the second glass tube, as in the two cases quoted from Table V. before retardation occurs. If, on the other hand, the rubber be either very long or very thin, the time may be insufficient for the flame front to reach the second glass tube before it is retarded (e.g., 6.3 per cent. C_2H_4 in O_2 under the conditions given in Table IV.).

In some experiments it was noted that the flame in the second glass tube had an initial velocity slightly less than that in the first glass tube, and that the speed increased gradually until the normal detonation rate for the mixture was re-established. Such a case is illustrated in Fig. 6 for the mixture $2\text{H}_2 + \text{O}_2 + \text{SO}_2$. It will be seen that the recovery to normal rate, accompanied by no abrupt change in luminosity, takes place without the production of a retonation wave such as is usually observed when a "slow" flame gives place to an explosion wave. Such records may be explained by assuming that the expansion of the rubber has caused some small reduction in the pressure supporting the forward motion of the explosion wave. When, however, the flame enters the glass tube, expansion is no longer possible; pressure conditions, therefore, return gradually to normal and the velocity shows a gradual increase in accord with this. Although the flame shows a small temporary reduction in velocity, we suggest that the mode of propagation throughout is that of an explosion-wave; this would account for the absence of any retonation wave where normal velocity is restored.

Summary.

Photographs have been obtained by means of a rotating drum camera showing the behaviour of explosion waves on passing through a rubber section of a long explosion gallery. These records show that explosion waves in "non-striating" mixtures, e.g., $2\text{H}_2 + \text{O}_2 + \text{N}_2$, $\text{CH}_4 + 2\text{O}_2$, $2\text{CO} + \text{O}_2 + (7 \text{ per cent. } \text{H}_2)$, etc., can pass through considerable lengths of even very thin rubber tubing without any appreciable alteration in velocity: whereas those in "striating" mixtures, e.g., $2\text{CO}_2 + \text{O}_2$, $2\text{H}_2 + \text{O}_2 + \text{CO}_2$, $\text{CH}_4 + 7\text{O}_2$, on passing through the rubber, may show a marked reduction in flame velocity, which is dependent upon such factors as thickness and length of rubber.

It is suggested that the observed reduction in velocity may be due to release of pressure behind the wave front. At the present stage no attempt is made to explain the difference in behaviour between "striating" and "non-striating" mixtures. It is hoped, however, to offer, shortly, a more detailed consideration of these and other closely related experiments.

The authors wish to express their thanks to Mr. John Harwood, M.Sc., for helpful criticism and to acknowledge the receipt of a grant from Imperial Chemical Industries, Ltd., toward the cost of the investigations.

*Chemical Department,
The University,
Manchester.*

THE QUANTUM YIELD IN THE PHOTO-DECOMPOSITION OF THE ALKYL HALIDES IN NON-POLAR SOLVENTS.

BY WM. WEST AND BEATRICE PAUL.

Received 21st June, 1932.

The ultra-violet spectra of the methyl halides in the gaseous state are characterised by a region of continuous absorption and, towards shorter wave-lengths, a spectrum showing discrete vibrational bands.¹ The spectrum of the iodide has the maximum of the continuous region at about 2530 Å. The continuous spectrum has also been found in the higher iodide vapours,² the maxima varying from 2550 Å. for isobutyl iodide to 2680 Å. for tertiary butyl iodide; the liquids show essentially the same type of absorption.^{3, 2} These continuous spectra are very similar in appearance to those of the hydrogen halides, which are evoked, according to current views, by an electronic excitation to a state in which the nuclei repel; and the assumption made by the various investigators of the alkyl halide spectra that the molecular process associated with the continuum is similarly a dissociation into a free alkyl radicle and a halogen atom, one or other of which may be in an excited electronic state, and which are disrupted from each other with considerable kinetic energy, seems very plausible.

This identity of absorption process in the alkyl halides is not, however, reflected in the details of the photochemical changes which these substances undergo. On exposure to ultra-violet light they all undergo decomposition with the liberation of iodine, but Burke and Donnan⁴ showed that the rate of their photo-reactions, like that of their thermal reactions, is determined by the nature of the radicle. It is true that no precautions were taken by these investigators to remove air, but the dependence of the photo-decomposition in the absence of

¹ G. Herzberg and G. Scheibe, *Z. physik. Chem.*, **B. 7**, 390, 1930.

² G. Emischwiller, *Compt. Rend.*, **191**, 208, 1930.

³ T. Iredale and W. N. W. Wallace, *Phil. Mag.* (vii.), **8**, 1093, 1929.

⁴ K. Burke and F. G. Donnan, *J.C.S.*, **85**, 574, 1904.

oxygen on the radicle has been substantiated by the later work of Job and Emschwiller.^{5, 6}

The quantum efficiency for the photo-decomposition of liquid ethyl iodide has been determined by Iredale,⁷ who observed a yield of about one atom of iodine produced per quantum absorbed by the ethyl iodide for a wave-length 3650 Å., and 1.2 for shorter wave-lengths in the region 2480 Å. to 3650 Å., the average quantum being taken as corresponding to wave-length 3100 Å.

The proximity of the value of the quantum yield to unity was taken to indicate a rather simple mechanism for the reaction, a conclusion which, however, is not supported by later work. Emschwiller⁶ reported low values for the "coefficient of utilisation" in the decomposition of various alkyl iodides in the liquid state by light of wave-length 3650 Å., without, however, specifically stating the quantum yields. Moreover, at this wave-length there was a marked increase in the value of this coefficient with temperature. The coefficient of utilisation was found to increase with shorter wave-lengths of the illuminating light and the temperature coefficient fell to a value no higher than 1.06 in a silica vessel exposed to the full light of the mercury arc.

In the light of the observation of Burke and Donnan⁴ that the rate of photo-decomposition for isopropyl iodide is considerably greater than that of propyl or ethyl iodides, a quantum efficiency of one for ethyl iodide might necessitate efficiencies in excess of two for iso-propyl iodide, an observation which, if verified, would require for its explanation the invocation of a chain mechanism in the decomposition of the compound. The result of Bates and Spence^{8, 9} that the photo-decomposition of gaseous methyl iodide takes place with a yield of the order 0.02 at 0° C. for light of the full mercury arc also points to the fortuitousness of the value one for ethyl iodide, and the inadequacy of this value as a basis for the supposition that the photo-decompositions of the alkyl iodides are essentially very simple reactions. We have, therefore, determined here the quantum efficiencies of the lower member of the alkyl iodide series. The reactions were performed in solution, since this permits easy study of the influence of concentration, and hexane was used as solvent, since its non-polar nature makes this solvent unlikely to have great influence on the course of the reaction.

Experimental.

Materials.—With the exception of vinyl iodide, all of the iodides used were commercial products of good quality, which were shaken with mercury for the shortest time necessary to remove free iodide, and fractionated after separation from the mercury. Immediately before each experiment, the necessary amount of iodide was distilled in a current of nitrogen from a portion of the stock quantity. The hexane was obtained from commercial hexane or from high boiling ligroin by fractionation and purification by the method of Castille and Henri.¹⁰ The product of boiling-point 65°-70° transmitted the continuous hydrogen spectrum to 2000 Å., and though, of course, it was a mixture of

⁵ A. Job and G. Emschwiller, *Compt. rend.*, **179**, 52, 1924.

⁶ G. Emschwiller, *Ibid.*, **190**, 866, 1930.

⁷ T. Iredale, *J. Physic. Chem.*, **33**, 290, 1929.

⁸ J. R. Bates and R. Spence, *J.A.C.S.*, **53**, 1689, 1931.

⁹ *Ibid.*, *This Journal*, **27**, 468, 1931.

¹⁰ A. Castille and V. Henri, *Bull. Soc. Chim. Biol.*, **6**, 299, 1924.

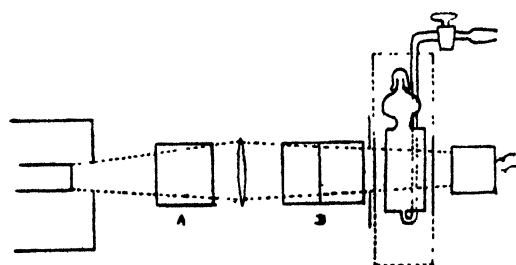
isomers, no difference in the course of the reactions was observed with different batches of solvent, purified from different samples of the crude material.

Vinyl iodide was prepared by the action of sodium ethoxide on ethylene diiodide, obtained by passing ethylene into a suspension of iodine in 95 per cent. ethyl alcohol. We are indebted to Dr. John Spence of this department for his preparation of this substance by a modification of the method of producing unsaturated compounds which gives a yield of vinyl iodide approximately twice that previously reported in the literature, as will be described in a future volume of the publication, "Organic Synthesis."

Order of the Reaction.—If the absorption of the light is complete, the decomposition should be of zero order, except in so far as the reaction is inhibited by the accumulation of products, either owing to their absorbing light or otherwise. A molar solution of *n*-propyl iodide in hexane in a layer of the thickness (2 cm.) used in the experiments on quantum efficiency was found by photography of the continuous hydrogen spectrum to absorb all radiation of wave-length shorter than 3300 Å. The presence of *N*/2000 iodine in this solution caused all wave-lengths short of 3400 Å. to be absorbed, although a solution of iodine of this concentration in pure hexane was transparent in the ultra-violet down to 2500 Å. It is evident that the iodine may be absorbing in the region to which the alkyl iodides are photo-sensitive. To test the deviations from a zero order reaction which might thus be caused, a 250 c.c. quartz flask was blackened on the upper half, filled with a solution of the iodide, and exposed, with elimination of oxygen and stirring by means of a current of nitrogen, to the unfiltered light of a mercury arc. The blackening of the upper half allowed the withdrawal of portions of solution for analysis without the introduction of changing surfaces in the illuminated volume. Portions were withdrawn from time to time and the iodine analysed by titration with *N*/200 thiosulphate, the disappearance of the pink colour being taken as the endpoint. A 0.05*N* solution of ethyl iodide decomposed linearly with time within the limits of error until the concentration of iodine produced was about 0.001*N*, while the highest concentration of iodine produced in the measurements of the efficiency was about 0.0005*N*; deviations from linearity occurred when the concentration of iodine produced was greater than 0.001*N*, amounting to some 15 per cent. when the concentration of iodine produced was 0.003*N*. The quantum efficiency as measured by the following experiments was therefore not sensibly influenced by the iodine produced.

Measurement of Quantum Yield.

The arrangement of apparatus is made obvious from the diagram.



Light from a quartz mercury lamp in the "end-on" position was projected by a quartz lens on the reaction cell, contained in a small air thermostat provided with two quartz windows. A diaphragm placed before the front window of the thermostat limited the beam so that

the whole beam just covered the active surface of the thermopile. A and B were quartz cells containing suitable filters. The quartz reaction vessel, 2 cm. thick, with plane windows $3\frac{1}{2}$ cm. in diameter, was provided with a capillary inlet through which hydrogen could be bubbled. The thermostat contained a small motor-driven fan for the equalisation of temperature, and a Beaver thermostat control¹¹ permitted the temperature to be easily maintained constant to $1/20^\circ$.

The large Moll surface thermopile was used in conjunction with a Moll galvanometer shunted with 50 ohms. The thermopile-galvanometer system was calibrated at intervals by means of a Bureau of Standards carbon filament lamp; during the several months occupied by the experiments, the calibration did not alter appreciably.

In all experiments, the cell A, 5 cm. thick, of fused quartz with plane windows, contained bromine at its saturation pressure at 20° C. To obtain the region near the maximum of absorption of the halides, the cell B was made up of two cells cemented together, one containing a thickness of 3 cm. of *n*-acetic acid, the other 3 cm. thickness of chlorine at atmospheric pressure. This combination transmitted in the ultra-violet between the strong Hg. line 2805 Å. and 2500 Å., the chief line being 2800 Å., 2654 Å., and 2537 Å. in the ratio of 2 : 24 : 37, the centre of gravity of the region being about 2610 Å. The bromine suppressed the violet and blue lines, and a considerable fraction of the green and yellow. To obtain a wave-length nearer the beginning of the absorption of the halides, 3 cm. thickness of a solution of potassium chromate of concentration 0.2 gm./l. in dilute alkali was interposed in position B. This transmitted the strong Hg line at 3130 Å. well, with a relatively small fraction of the line at 3030 Å. No great error will be incurred by assuming the effective quantum that corresponding to wave-length 3130 Å. Since the reaction is influenced by oxygen, the yields were determined in an atmosphere from which oxygen had been as far as possible removed. Immediately before each experiment, a quantity of hexane was rapidly distilled in a current of nitrogen, collected warm and transferred to the reaction cell through which was bubbling a rapid stream of hydrogen freed from oxygen by passing over red-hot copper and dried by magnesium perchlorate. The bubbling of the hydrogen through the hexane was continued for about an hour, while the lamp was attaining its steady state, being interrupted occasionally in order to read the galvanometer deflection. The iodide was similarly distilled in nitrogen immediately before its addition to the hexane, added, the bubbling of hydrogen continued for about ten minutes, and the cap, from which air had been displaced by hydrogen, then placed on the reaction cell. The galvanometer deflection was again measured, the difference in the mean values of the deflection before and after addition of the iodide corresponding to the energy absorbed by the iodide.

The strong Hg line in the near infra-red at 1.014μ is transmitted to the extent of about 30 per cent. by the thickness of aqueous solution used in the filters, but the following observations eliminate the possibility of its seriously disturbing the values of the quantum yield. Both hexane and the alkyl iodides have an absorption band in this neighbourhood, the maximum, however, of which is about 1.16μ and which falls off rapidly in both directions.¹² In fact, the thermopile caused a somewhat

¹¹ D. J. Beaver and J. J. Beaver, *Ind. Eng. Chem.*, **15**, 359, 1923.

¹² B. J. Spence and M. A. Easley, *Physic. Rev.*, **34**, 730, 1929.

greater deflection when the light from the arc was transmitted through the reaction cell filled with hexane than through the empty cell, indicating that absorption by hexane is at most small and is more than compensated by the diminished reflection at the hexane-quartz surfaces compared with air-quartz surfaces. It was also shown by direct photography of the Hg line 1.014μ in the second order of a metre grating on the very fast infra-red plates recently introduced by the Eastman Kodak Company¹³ that the density of this line was only slightly decreased on the introduction of hexane into the reaction cell and was not further changed by the addition of ethyl iodide at the greatest concentration used in the measurements of the yield.

To test the optical arrangement and thermopile calibration, two determinations were carried out of the quantum yield, for light transmitted by the chlorine-bromine-acetic acid filter, in the hydrolysis of 0.5 *n*-monochloroacetic acid, for which a value of unity has been found by Rudberg,¹⁴ at wave-length 2537 Å. The chloride ion produced was determined by titration with *N*/200 AgNO₃ measured by means of a micro burette.

The results of the experiments are shown in Table I:—

TABLE I.

Date.	Time of Exposure.	No. of Quanta Absorb.	No. of Cl Produced.	Yield.
1/2/32	20 hrs. 10 min.	2.34×10^{18}	2.14×10^{18}	0.92
2/3/32	27 hrs. 10 min.	5.07×10^{18}	4.83×10^{18}	0.95

In the calculation of these yields no correction has been made for reflection of light at the rear surface of the reaction vessel nor at the rear quartz window of the thermostat. Since the value of one for the efficiency in this reaction seems to be well substantiated, we have assumed that neglect of this correction is largely compensated by other errors in the energy measurements, such as lack of uniformity in the surface sensitivity of the thermopile, and the yields reported for the iodide decompositions have not been corrected nor adjusted in any way.

The quantum efficiencies for the decomposition of the alkyl halides were determined with reference to the number of iodine atoms produced per quantum absorbed. The determination of the iodine produced was carried out by titration with *N*/200 thiosulphate, measured out from a micro-burette graduated in twentieths of a cubic centimetre and capable of being estimated to ± 0.1 c.c. The volume of thiosulphate required was usually about 2 c.c. As indicator, the colour of the iodine itself was used, as the presence of alkyl iodide interferes with the starch coloration, and direct experiment showed that two equal volumes of the same iodine solution, one in aqueous potassium iodide solution containing starch, the other in hexane solution containing 10 per cent. propyl iodide, required the same volume of thiosulphate to reach the end point, as determined by the disappearance of the blue and pink

¹³ C. E. K. Mees, *J. Opt. Soc. Amer.*, **21**, 753, 1931.

¹⁴ E. G. Rudberg, *Z. Physik*, **24**, 247, 1924.

colours respectively. The determinations were made for the mean wave-lengths 2610 Å. and 3130 Å., at temperatures 25° and 35° C. and for concentrations of the alkyl iodides varying from 0.005 to 1.78 molar. At all these concentrations absorption of the effective light is complete.

Results.

TABLE II.

Substance.	Concentration, Mols./Litre.	Temp. °C.	Length of Exposure.	Quanta Absorbed $\times 10^{-18}$.	Atoms of Iodine Produced $\times 10^{-18}$.	Yield.
Mean Wave-length 2610 Å.						
Methyl iodide .	1.78	25	Hrs. Min.			
"	1.78	25	9 43	42.4	1.75	0.041
"	1.78	25	4 37	17.5	0.79	0.045
"	1.78	25	4 46	11.7	0.67	0.057
"	1.78	35	6 11	18.0	1.09	0.060
"	1.78	35	5 35	18.6	1.06	0.057
					Mean	0.052
Ethyl iodide .	1.38	25	4 10	13.2	8.26	0.63
"	1.38	25	2 30	8.50	4.86	0.57
"	1.38	35	2 51	7.70	4.20	0.55
"	1.38	35	3 22	7.62	4.51	0.59
"	0.33	35	5 9	10.0	5.47	0.55
"	0.007	35	3 55	7.12	4.10	0.58
					Mean	0.58
Vinyl iodide .	1.50	25	6 41	12.9	5.75	0.45
"	1.50	25	4 38	12.7	5.47	0.43
"	1.50	35	3 16	8.58	3.87	0.45
"	1.50	35	4 36	11.2	5.5	0.49
					Mean	0.46
n-propyl iodide .	1.15	25	5 44	9.27	4.86	0.52
"	1.15	25	2 44	9.30	7.00	0.75
"	1.15	25	2 17	8.15	6.24	0.76
"	1.15	25	5 17	17.4	10.9	0.64
"	1.15	35	4 47	8.72	6.45	0.74
"	1.15	35	4 6	10.1	6.81	0.68
					Mean	0.68
iso-propyl iodide .	1.1	25	1 41	5.35	6.2	1.16
"	0.83	25	1 35	4.46	5.0	1.12
"	1.1	35	3 22	8.02	9.15	1.14
"	0.93	35	2 52	6.0	7.56	1.25
"	0.28	35	2 14	3.74	4.23	1.13
"	0.13	35	4 0	7.76	7.58	0.98
"	0.065	35	2 18	3.52	4.20	1.19
"	0.005	35	2 9	2.98	3.65	1.22
					Mean	1.15
Allyl iodide .	1.22	20	6 15	30.3	2.12	0.070

TABLE II.—(continued).

Substance.	Concentration. Mols./Litre.	Temp. °C.	Length of Exposure.	Quanta Absorbed $\times 10^{-18}$.	Atoms of Iodine Produced $\times 10^{-18}$.	Yield.
Mean Wave-length 3130 Å.						
Methyl iodide .	1.78	28	19 0	38.5	0.304	0.0081
Ethyl iodide .	1.38	25	12 0	22.8	7.26	0.32
"	1.38	25	8 46	17.5	5.26	0.30
"	1.38	35	4 20	9.40	2.58	0.27
"	1.38	35	3 45	7.71	2.43	0.31
					Mean	0.30
Vinyl iodide .	0.94	25	8 28	16.1	2.43	0.15
"	0.94	35	12 0	25.0	3.80	0.15
					Mean	0.15
n-propyl iodide .	1.15	25	8 2	17.1	5.41	0.32
"	1.15	25	12 53	25.3	8.21	0.32
"	1.15	35	14 7	20.2	6.38	0.31
"	1.15	35	13 49	23.4	8.24	0.35
"	1.15	35	9 27	18.9	6.60	0.35
					Mean	0.33
iso-propyl iodide .	1.10	25	11 40	15.3	9.39	0.61
"	1.10	25	7 10	12.80	7.60	0.59
"	1.10	25	4 14	8.70	4.96	0.57
"	1.10	35	4 2	7.81	5.63	0.72
"	0.22	35	4 30	5.90	3.80	0.65
"	0.22	35	12 15	16.0	10.3	0.65
					Mean	0.65

The results which are exhibited in Table II. may be summarised thus :

1. The quantum efficiency of the photochemical dissociation of the alkyl iodides in hexane solution is a constitutive property, and varies with the compound from a value of a few hundredths to slightly over one. Of the group studied, methyl iodide has the lowest yield and *iso*-propyl the highest.

2. The quantum efficiency increases with diminishing wave-length of the illuminating light between 3130 Å. and 2610 Å. The ratio of the values of the yield at 2610 Å. to that at 3130 Å. is 6.5 for methyl iodide, 1.9 for ethyl iodide, 2.9 for vinyl, 2.1 for *n*-propyl iodide, 1.8 for *iso*-propyl iodide.

3. Within the limits of experimental error, the quantum efficiency is not altered by an increase in temperature from 25° C. to 35° C. for illumination by light of these wave-lengths.

4. The quantum efficiency is independent of the concentration of alkyl iodide, and up to the concentration of iodine produced in the experiments, is uninfluenced by this product.

The value of 0.070 for allyl iodide is subject to some uncertainty, owing to the possibility of the presence of impurity. Allyl iodide oxidises extremely readily in air, and is not easy to distil without separation of iodine even in a current of nitrogen. The material used, being still pale brown after a distillation in nitrogen, was shaken up for

a moment with mercury, a procedure which left a pale yellow product, retaining its colour after distillation in nitrogen. As allyl iodide forms a volatile compound with mercury it is possible that the product obtained in this way contained mercury. There is no doubt, however, of the extreme slowness of the photo-decomposition, in the absence of oxygen, of the allyl iodide thus obtained, compared with the decomposition under the same circumstances of, say, ethyl iodide, or with the very rapid change which occurs on illuminating allyl iodide, similarly purified, in the presence of air. Vinyl iodide also oxidises with the separation of iodine more readily than the saturated compounds, but here no difficulty was experienced in obtaining a colourless product by distillation, nor is the yield in the photo-decomposition very much lower than for ethyl iodide.

Influence of Oxygen.

Since Bates and Spence⁸ have found a yield for the photo-oxidation of methyl iodide vapour some hundred times greater than for the photo-decomposition in the absence of air, it is of some importance to determine the possible influence of traces of oxygen on the results of the experiments here reported. A 1.38 molar solution of ethyl iodide in hexane, illuminated at 25° C. with light of wave-length 2610 Å., as previously described, but in an atmosphere of pure oxygen, yielded exactly 2 atoms of iodine for every quantum absorbed, a value which happens to be close to that obtained by Bates and Spence in the photo-oxidation of methyl iodide vapour. As the ratio of the oxidation to the decomposition in the absence of oxygen for ethyl iodide solution is only 4 : 1, in view of the precautions taken to remove oxygen, no great error seems likely to be introduced into the values found for the yield in the dissociation owing to accidental presence of oxygen, a conclusion which it seems reasonable to extend to the other compounds studied.

Influence of Absorbing Inert Solvent.

It seemed of some interest to investigate the yield for the photo-decomposition of these substances in a solvent which, like hexane, has little or no permanent electric moment, but which possesses an absorption band in the region absorbed by the iodides. The well-known banded spectrum of benzene is in the proper region for this purpose. An experiment was performed with a 0.03 molar solution of ethyl iodide in this solvent, exposed to the light transmitted by the chlorine-bromine-acetic acid filter—with the following result. Total number of quanta absorbed by solution = 23.5×10^{18} . Number of iodine atoms produced = 12.2×10^{18} . Yield = 0.52, in substantial agreement with the value 0.58 in hexane solution. It is very evident that the benzene is not acting as an inner filter; for, taking from Scheibe's curve for the absorption coefficient of ethyl iodide in hexane solution¹⁵ the value of 200 as representing approximately the mean value for the illuminating light used, and assuming that it is not much changed in benzene, and taking from Henri's curve the value 100 for benzene,¹⁶ and considering that the ratio of molar concentrations of ethyl iodide to benzene was 0.03 to 11.2, one obtains that the ratio of probability of absorption of ethyl iodide molecules to that by benzene molecules is about 1 to 180. In

¹⁵ G. Scheibe, *Ber.*, **58**, 592, 1925.

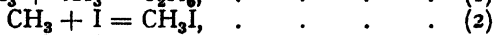
¹⁶ V. Henri, *Études de Photochimie*, **115**, Gauthier-Villars et Cie, Paris, 1919.

the experiment the benzene was added to the cell first and it was in fact observed that there was no further measurable diminution in the galvanometer deflection on the addition of the ethyl iodide. This appears to be another case of the kind of optical sensitisation found by Weigert and Prukner¹⁷ in the transformation of *o*-nitro-benzaldehyde to *o*-nitroso-benzoic acid in acetone solution, for which the yield is the same in a part of the spectrum in which the acetone absorbs most of the light as in a region in which practically all of the absorption is due to the aldehyde, a fact from which these authors make the generalisation that in the presence of several absorbing substances there is no photo-chemical equivalent to Beer's Law, but that with respect to the photo-chemical change, the whole of the energy absorbed by the system is available.

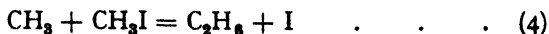
Discussion.

The assumption that the process associated with the absorption is a dissociation into a free radicle and an iodine atom, one of which may be excited, and which part from each other with considerably greater kinetic energy than the most probable value corresponding to the temperature, is in accord with the type of spectrum exhibited by the alkyl halides. The primary process $\text{CH}_3\text{I} + h\nu = \text{CH}_3 + \text{I}$ would then have a yield of unity. The departure of the experimental values from this value must be due to secondary processes, such as have been considered by Bates and Spence.^{8, 9} What these secondary actions may be cannot be determined from measurements of the quantum yield made with respect to the quantity of iodine produced alone, but certain possibilities seem excluded by the present results.

Obvious secondary reactions are

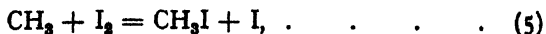


which, necessitating three body collisions, might not occur very frequently in the gaseous phase, but which in solution might occur readily. It is also possible that a free radicle might react with a molecule of alkyl iodide,



in a manner analogous to the reaction $\text{H} + \text{HI} = \text{H}_2 + \text{I}$ which follows the primary dissociation of HI. If every free alkyl group reacted in this way, the quantum yield would be 2. That this reaction does not occur very frequently, however, is indicated by the independence of the yield on the concentration of the alkyl iodide over a range of two hundred fold, a result which may be contrasted with the slow rise in yield from 1 to 2 with rise in concentration in the photolysis of HI in hexane solution.¹⁸

The reaction



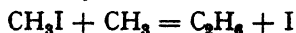
which is exothermic to the extent of some 6 or 7 cal. and which would tend to diminish the yield, does not seem to be frequent, as shown by the zero order of the reaction in its early stages. When sufficient iodine has accumulated, however, there is a diminution in yield, possibly due either to this reaction or to absorption of light by the iodine.

¹⁷ F. Weigert and F. Prukner, *Z. physik. Chem., Bodenstein Festband*, 1931.

¹⁸ E. Warburg and W. Rump, *Z. Physik*, 47, 305, 1928.

The gaseous products of the decomposition of liquid ethyl iodide, as reported by Job and Emschwiller,⁸ are rather complicated, consisting of 53 per cent. ethylene, 36 per cent. ethane, 5 per cent. hydrogen and only 6 per cent. butane. It would seem that the reaction $2C_2H_5 = C_4H_{10}$ occurs much less frequently than $C_2H_5 + C_2H_5 = C_2H_4 + C_2H_6$. The addition of iodine to olefinic products is also a possible way in which the yield may be diminished.

The increase in yield with diminishing wave-length observed in these decompositions is paralleled by numerous other cases in solution and in some gaseous reactions. Again, the photolysis of the alkyl iodide differs in this respect from that of hydrogen iodide in hexane solution, where the yields for wave-length 2220 Å. are less than for wave-length 2820 Å.¹⁸ Had there been any evidence that the reaction



occurred, it might have been advanced that the greater kinetic energy of the radicle produced by the shorter wave-lengths caused this reaction to occur more often in these regions of the spectrum than towards the long wave limit of the band, with consequent increase in yield. But it seems more in accord with the independence of yield on the concentration of alkyl iodine to suppose that the increase in yield with diminishing wave-length is due to a suppression of the reunion of free radicles and iodine atoms, due to the greater velocity with which they are separated, and the consequently smaller time during which the two products linger in each other's neighbourhood.

If the main secondary reaction tending to diminish the yield is simply the recombination of the free radicle and the iodine atom, the values of the quantum efficiencies give the relative probabilities of combination of different alkyl groups with iodine atoms. The order of reactivity of alkyl radicles on this criterion, is

Methyl > allyl > vinyl > ethyl > propyl > isopropyl.

Summary.

The quantum efficiencies for the photo-decompositions of the lower members of the alkyl iodides in hexane solution in the absence of oxygen vary largely with the nature of the radicle, between a value of a few hundredths for methyl iodide to rather more than one for *iso*-propyl iodide.

The yield increases with diminishing wave-length in the region between 3130 Å. and 2610 Å., is uninfluenced by a 200-fold change in concentration of the iodide in the range 0.005 to 1 molar, and at these wave-lengths is independent of temperature.

There is no parallelism between readiness of oxidation and readiness of undergoing decomposition in absence of oxygen.

The employment, as a solvent, of benzene, which absorbs in the same region as the iodides, does not markedly diminish the yield.

If the deviations of the yield from values between 1 and 2 are ascribed principally to recombination of free alkyl groups and iodine atoms the efficacy of collisions with respect to the initiation of chemical reaction between free radicles and iodine atoms is in the order,

methyl > allyl > vinyl > ethyl > propyl > isopropyl.

*Department of Chemistry,
Washington Square College,
New York University, N.Y.*

THE HEAT OF FORMATION AND STRUCTURE OF THE CARBON-OXYGEN AND CARBON-SULPHUR LINKAGES.

BY W. LOCHTE-HOLTGREVEN * AND C. E. H. BAWN.

Received 27th June, 1932.

The heat of linkage in diatomic molecules can be determined directly and the process of dissociation followed in detail. In the case of polyatomic molecules our knowledge of the dissociation process is not so complete. Although the dissociation has been determined spectroscopically in some cases, the heats of linkage in polyatomic molecules are usually evaluated from the thermochemical heat of formation of the molecule from its elements. This method depends on the assumption that the heat of any linkage is independent of the other linkages in the molecule, and has led to consistent values for the energies of many links. This assumption however cannot be generally true, as will be shown later. In the present work the energy of the CS and hence the CO linkage in carbonyl sulphide has been determined by photo-chemical methods and the absolute energy values of these linkages have been calculated. These values have been compared with these of the CS and CO bonds in similarly formed molecules and some conclusions with respect to the valency of the carbon atom and the structure of these molecules have been drawn. The relationship of the force constant to the type of the linkage has been discussed in detail for a number of molecules.

Experimental.

Carbonyl sulphide was prepared by dropping a concentrated solution of potassium thiocyanate on to sulphuric acid (290 c.c. in 400 c.c. water). The gas contained about 2 per cent. carbon dioxide and small quantities of carbon disulphide, hydrogen sulphide and possibly hydrogen cyanide. It was purified by passing through 33 per cent. caustic potash and the carbon disulphide removed by adsorption with freshly ignited wood charcoal. The gas was dried with phosphoric oxide and was stored over mercury and mercuric oxide for several days before use, in order to remove the last traces of hydrogen sulphide and hydrogen cyanide. Without careful purification the absorption spectrum showed faint traces of a banded structure, but with the pure gas this disappeared.

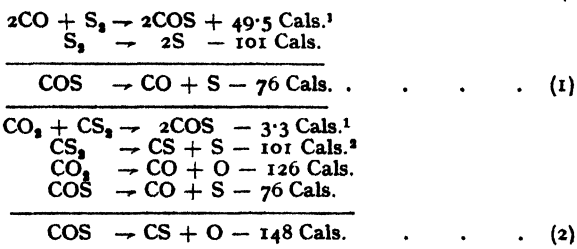
The absorption cell was a glass tube 4 cm. in diameter and 1 metre in length, with ground quartz windows. The system for evacuation consisted of a two-stage mercury vapour pump and oil pump, the pressure in the tube being measured by a mercury manometer. The spectrum was photographed with a quartz spectograph giving a dispersion of 12.5 Å./mm. at 2500 Å. A water-cooled hydrogen discharge tube was used as a source of light and a copper spark employed as a comparison scale.

Results and Discussion.

The spectrum of the pure gas showed a complete transparency to 2550 Å., at which point a strong continuous absorption appeared starting

* John Harling Fellow, University of Manchester.

from a sharp edge and extending towards the violet. The absorption limit for a series of pressures was determined graphically from direct photometric measurements and found to be at $2550 \pm 20 \text{ \AA}$. The spectrum is interpreted as corresponding to the dissociation of the carbonyl sulphide molecule. The products of dissociation are CO and S or CS and O, one of which, in each case, may be in the excited state. The dissociation energies as calculated from thermochemical data are 76 and 148 Cals. respectively.



The determined photochemical dissociation energy is 4.84 volts or 111 ± 1 Cals. and hence the dissociation must proceed according to (1). This was also indicated by a deposition of sulphur on the walls of the absorption tube. The difference between the photochemical and the thermal value is the excitation energy of the carbon monoxide molecule or the sulphur atom. Since the lowest excitation potential of the carbon monoxide molecule is 5.9 volts above the ground level it is suggested that the sulphur atom is excited. The lowest possible excitation energy corresponds to the difference between the 3P ground level and the 1D metastable state. The position of the latter term has not hitherto been fixed from the S spectrum. By analogy with the oxygen atom (corresponding energy 1.96 volts) McLennan and Crawford³ suggested 1.2 volts for the position of this term. The latter value, however, may not be accurate as has been shown from general considerations by Frerichs.⁴ Christy and Naudé⁵ have recently determined the predissociation spectrum of sulphur and give a value of 1.6 volts for this energy difference. This is in satisfactory agreement with the above experimental value.

Heat of Linkage of the CO and CS Bond.

It is generally accepted that both carbon dioxide and carbon disulphide have a symmetrical linear structure. Recent investigations by Bailey and Cassie⁶ and Kohlrausch⁷ on the infra-red and Raman spectra of carbonyl sulphide indicate that this molecule is intermediate in its structure between carbon dioxide and carbon disulphide. A linear triatomic molecule XYX has three fundamental frequencies of vibration. Assuming that increased vibrational energy leads to dissociation of the molecule, it is clear that only the most unsymmetrical vibration ν_2 (or a combination of ν_2 and ν_3) can lead to XY and X as the products of dissociation. If dissociation followed from ν_1 and ν_3

¹ Stock, *Ber.* **57**, 719, 1924.

² Landolt-Börnstein Tabellen, vol. 5, 1019.

³ McLennan and Crawford, *Nature*, **124**, 874, 1929.

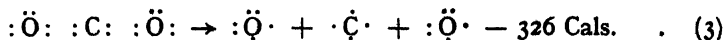
⁴ Frerichs, *Physic. Rev.*, **36**, 406, 1930.

⁵ Christy and Naudé, *Physic. Rev.*, **37**, 907, 1931.

⁶ Bailey and Cassie, *P.R.S.*, **135 A**, 375, 1932.

⁷ Kohlrausch, *Physikal. Z.*, **33**, 165, 1932.

directly the products would be $2X$ and Y . As an example of the latter type we may consider the ideal dissociation of carbon dioxide such that both oxygen atoms are removed simultaneously as in (3)



The products will be two normal oxygen atoms and a quadrivalent carbon atom (in the 5S metastable state). The thermochemical value for the complete dissociation into normal atoms is 363 Cals. This is greater than required in (3) by an amount equal to the excitation energy of carbon atom. This energy, the difference between the 3P state (ground state of the triplet system) and the 5S state (ground state of the quintet system) is about 1.6 volts or 37 Cals.

The energy required for the process (3) is therefore $363 - 37 = 326$ Cals. Since the carbon dioxide molecule is symmetrical, this gives a value of 163 Cals. for the true heat of linkage of the $C=O$ bond, which is in agreement with the energy of the $C=O$ bond in aldehydes and ketones (page).

Carrying out the same process with the carbon disulphide molecule, the corresponding values are 263 Cals. (heat of formation*) - 37 Cals. leaving 113 Cals. for each $C=S$ bond. The same values for the bond energies satisfy the carbonyl sulphide molecule. The energy of dissociation by a process similar to (3) is $310 - 37$ Cals. = 273 Cals., which is the sum of the absolute heats of linkage of the $C=O$ and $C=S$ bonds ($113 + 163$ Cals.).

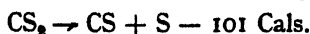
It must be emphasised that the complete dissociation in one stage, although the bonds in symmetrically formed molecules are equal, is essentially different from carrying out the dissociation in two steps. The splitting of the first bond requires a different energy according to the rearrangement of the electronic configuration in the remainder of the molecule. Thus the splitting of the first oxygen from the carbon dioxide molecule needs only 126 Cals., leaving 237 Cals. for the remaining CO bond. This is the same as the dissociation energy of the carbon monoxide molecule into normal atoms as determined from band spectra. It seems therefore that a valency rearrangement takes place after the removal of the first oxygen atom to give a triple bond between the carbon and the oxygen, as is normally assumed in the carbon monoxide molecule. On the other hand, although the structure of carbon monoxide is usually given as $C \equiv O$, the bond must still be attributed to a divalent carbon atom in the 3P state.† The third link, however, may be co-ordinate as indicated by dipole moment measurements.‡ Furthermore, the same value for the $C \equiv O$ bond is obtained from the dissociation energy of the carbonyl sulphide molecule. The dissociation into carbon monoxide and a normal sulphur atom requires 76 Cals., leaving 237 Cals. for the $C \equiv O$ bond.

* The heats of formation of the CS_2 and COS molecules are taken from a paper by Bailey and Cassie, *Proc. Roy. Soc.*, 135 A, 375, 1932.

† Mecke has suggested (*Leipziger Vorträge*, p. 37, 1931), that in the representation of the chemical bond the number of electrons contributed by each element should be shown. Thus he gives the formula of carbon monoxide as $C(4 + 2)O$, that is, the carbon contributes four electrons. This is not in agreement with the above view, and it seems necessary to write the formula $C(2 + 4)O$ since firstly, the products of dissociation are normal (not quadrivalent) carbon and oxygen; and secondly, the similarity between CO and N_2 shows that the oxygen provides the two electrons of the co-ordinate link.

‡ Hammick, New, Sidgwick and Sutton, *J.C.S.*, 1876, 1930.

The corresponding value for the carbon disulphide molecule is



Since the total heat of formation is 263 Cals. the energy of the remaining CS linkage is 162 Cals. From band spectra analysis of the CS bands an upper limit to the dissociation energy of 192 Cals. is obtained. Closer agreement may not be expected since the linear extrapolation was carried out over a wide region. The same energy (162 Cals.) is obtained from the dissociation of the carbonyl sulphide molecule. The splitting of the oxygen atom requires 148 Cals., and thus the CS bond energy is $310 - 148 = 162$ Cals. By analogy with the $\text{C} \equiv \text{O}$ this corresponds to the energy of the $\text{C} \equiv \text{S}$. The heats of linkage are summarised in the following table.

TABLE I.

Bond.	Molecule.				Absolute Value.
	CO_2	COS.	CS_2	$\text{H}_2\text{CO.}$	
$\text{C}=\text{O}$	126	148	—	155	163 Cals.
$\text{C}=\text{S}$	—	76	101	—	113 Cals.
<hr/>					
	$\text{C}=\text{O}$ 237 Cals.		$\text{C}-\text{O}$ 70.5 Cals.		
	$\text{C} \equiv \text{S}$ 162 Cals.		$\text{C}-\text{S}$ 58.7 Cals.		

The energy of dissociation of the $\text{C}=\text{O}$ bond in formaldehyde as determined photochemically⁹ is 155 Cals.



The value is higher than that of the $\text{C}=\text{O}$ energy in carbon dioxide and carbonyl sulphide since the hydrogen atoms have very little influence on the vibration of the CO group. The dissociation energy would therefore be expected to approach the absolute value of the bond.

The last values in Table I. are the dissociation energies of the singly linked carbon-oxygen and carbon-sulphur bonds as found in dimethyl ether and dimethyl sulphide.¹⁰ Neglecting the influence of the hydrogen atoms the values of 71 and 59 Cals. respectively can be regarded as close approximations to the true link energies of the single bond. It follows therefore that the absolute energy value of the double link is approximately twice that of the single link and that of the triple bond three times that of the single link.*

Valency and Force Constants.

Up to recent times interest in the chemical valency bond has been directed mainly to a clear understanding of the structure and saturation of the bond. The question has continually arisen as to whether we can assign to each valency bond a definite bond strength. In this respect valuable contributions have been obtained by spectroscopic methods

⁹ Herzberg, *Trans. Far. Soc.*, **27**, 378, 1931.

¹⁰ Sidgwick and Bowen, *Annual Reports*, p. 401, 1931.

* A similar relationship has previously been found by Bailey and Cassie (*loc. cit.*)⁶ for the force constants.

and numerous studies of the Raman effect have led to a simple classification of the various types of linkage which occur in molecules. These have been divided into two classes, (1) those links, the frequencies of which vary only slightly in different molecules, and (2) those whose frequencies are essentially dependent on the structure of the molecule, the so-called "inner" and "outer" vibrations respectively.¹¹ This classification, however, is quite arbitrary since the same type of linkage may in some compounds be an "inner" and in others an "outer" vibration. For example, the C=O group in all ketones gives rise to approximately the same frequency at 1700 cm.⁻¹, that is the group vibrates as a unit against the remainder of the molecule. On the other hand, in the carbon dioxide molecule the CO vibration is greatly influenced by the presence of the second oxygen. There is no longer a single CO vibration but the molecule vibrates as a whole involving two CO frequencies. In order to obtain some idea of the strength of binding of a given link it has been general to calculate the value of the force constant (restoring force per unit displacement) from the frequency of vibration.* This has led to the interesting result that the force constants of the frequencies of the inner vibrations of the lighter elements have approximately the same value for the same type of link, and the force constant of the double bond is twice and that of the triple bond three times as strong as the single bond. (Table II.).

TABLE II.

Bond.	Force Constant.	Bond.	Force Constant.	Bond.	Force Constant.
C—C	4.40	C—O	5.0	C—N	4.5
C=C	11.0	C=O	11.7	—	—
C≡C	16.4	C≡O	18.8	C≡N	19.2

Although these simple relationships have been of great value in determining the type of linkage, it should be pointed out that the application of this result is confined to the lighter elements of the first period of the periodic table. With the heavier elements, apart from their larger bond separation, it is necessary to consider the greater polarisabilities of the atoms. This brings about a marked change in the force constants of otherwise similar linkages. For example, the force constants of the halogen elements show a fourfold decrease from fluorine to iodine. Similar decreases are observed in other series of elements (Table III.). From a consideration of the above results it is apparent that the force constant has not a characteristic value for the single and double bond respectively.

¹¹ Kohlrausch, *Der Smekal-Raman Effect*, Berlin, 1931.

* Kohlrausch prefers to use the "mean restoring force," that is, the product of the force constant and the amplitude of vibration. However, the conclusions drawn in this paper regarding the force constants of molecules apply equally well to the "mean restoring force." On the other hand, Mecke characterises the bond by *Bindungswert*, i.e., the work required to double the atomic separation. These values are determined by the electronic configurations of the molecules, and have approximately the same values for corresponding molecules or compounds, for example the *bindungswert* for the halogens are F—F 36.6, Cl—Cl 40.4, Br—Br 40.9, I—I 37.8 volts. The value of the *Bindungswert* is not, however, a finite constant for the single, double or triple bond, but depends on the electron affinity of the constituents of the molecule.

TABLE III.

Molecule.	Force Constant.*	Molecule.	Force Constant.
	dynes/cm.		dynes/cm.
F—F	7.11×10^5	O = O	11.4×10^5
Cl—Cl	3.23 "	S = S	4.95 "
Br—Br	2.44 "	Se = Se	3.47 "
I—I	1.69 "	Te = Te	2.46 "

A similar variation of the force constant is found with many other atomic linkages of the same valency type. Some typical results are given in Table IV.

TABLE IV.

Molecule.	Force Constant.	Molecule.	Force Constant.
	dynes/cm.		dynes/cm.
C = O	14.2×10^5	C \equiv O	18.8×10^5
C = S	6.9 "	Si \equiv O \uparrow	9.1 "
S = O	7.74 "	—	—

Bailey and Cassie (*loc. cit.*)⁶ have concluded that the values of the force constants of the CS linkage indicate a single linkage between the carbon and the sulphur and that the formation of multiple bonds is confined to elements of the first period. This is not in agreement with the usual chemical conception of the sulphur double bond. The sulphur molecule appears to be similar to the oxygen molecule in every respect. The binding properties are identical, both molecules having a $^3\Sigma$ ground state indicating two unshared electrons. Furthermore, according to the theory of "binding" and "loosening" of electrons of Herzberg¹² the bond in each case is doubly linked. The observed decrease in the magnitude of the force constant of the C = S linkage compared with that of the C = O linkage can be explained by the decrease of the force constant for the double link from oxygen to tellurium as shown in Table IV.

Structure of Carbon Dioxide, Carbon Disulphide, and Carbonyl Sulphide Molecules.

In a recent paper on the analysis of the vibration types of simple molecules Mecke¹³ suggests that the CO bonds in carbon dioxide and carbon monoxide are similar in nature and assumes that the smaller energy necessary to split off the first oxygen atom from the carbon

* These values are directly comparable, since they refer (with the exception of fluorine) to the same electronic states of the molecule, *viz.*, $^1\Sigma$ ground state. The corresponding level for fluorine is accepted to be $^1\pi$, but this is doubtful, since no absorption measurements on this gas have been made. The force constants have been calculated from ω as obtained from band spectra data.

\uparrow The similarity of these molecules is evident from band spectra. The resonance transitions in both molecules are $^1\pi \rightarrow ^1\Sigma$ indicating similar electronic configurations (Saper, *Physic. Rev.*, 40, 465, 1932).

¹² Herzberg, *Leipziger Vorträge*, 1931.

¹³ Mecke, *Z. physik. Chem.*, 16, 409, 1932.

dioxide molecule results from the polarisation forces of the second oxygen atom. Mecke neglects the excitation energy of the carbon atom, and gives a structure for carbon dioxide which involves two triple bonds. The electronic configuration of the carbon monoxide molecule is identical with that of the nitrogen molecule and contains a triple linkage, although the carbon atom is still in the divalent state (page). In the carbon dioxide molecule the carbon atom is at least quadrivalent and the possible structures are $\ddot{\text{O}}::\text{C}::\ddot{\text{O}}$ and $:\text{O}::\text{C}::\text{O}:$. In support of the latter, Mecke assumes that the dissociation of the carbon dioxide molecule gives an excited oxygen atom and a normal carbon monoxide molecule, and this is necessary to give him the correct energy balance. This does not occur since Herzberg¹⁴ has recently shown that the dissociation takes place by a process analogous to predissociation and gives normal atoms. The first structure seems the more likely and agrees with the values of the heats of linkage and the force constants of the bonds. In the same manner it is concluded that all the linkages in carbonyl sulphide and carbon disulphide are double bonds. This is supported by the recent work of Pauling¹⁵ in which it is shown that two double bonds must of necessity be at 180° to one another and that the structures $\text{O}=\text{C}-\text{S}$ and $\text{S}-\text{C}-\text{S}$ cannot be linear.

Summary.

The photochemical dissociation of carbonyl sulphide leads to a normal carbon monoxide molecule and an excited sulphur atom in the 1D state (excitation energy 35 cal.).

The absolute values of the heats of formation of the $\text{C}=\text{O}$ and $\text{C}=\text{S}$ bonds in carbon dioxide and carbon disulphide have been calculated from the thermochemical heats of the ideal dissociation process, that is, complete dissociation in one stage. This process gives an excited carbon atom (1P), whereas the dissociation in two stages gives a normal carbon atom (3S). The wide variation in the heat of formation of the $\text{C}=\text{O}$ and $\text{C}=\text{S}$ bonds in different compounds is attributed to the influence of the neighbouring atoms on the normal vibrations. The $\text{C}=\text{O}$ bond energy in formaldehyde is approximately equal to the absolute value.

It is concluded that the value of the force constant is not a characteristic of the type of linkage, although this appears to be true for the elements of the first period. The force constants of corresponding linkages show a marked decrease with increasing atomic weight of the constituent elements.

The force constants and the heats of linkage of the CO and CS bonds in carbon dioxide, carbonyl sulphide and carbon disulphide show that all the bonds in these molecules are doubly linked.

In conclusion, the authors wish to express their thanks to Professor W. L. Bragg, F.R.S., for the kindness with which he placed every facility at our disposal, and to Mr. E. Eastwood for assistance with the experimental work of this paper.

*The University,
Manchester.*

¹⁴ Herzberg, *Z. physik. Chem.*, **17**, 68, 1932.

¹⁵ Pauling, *J.A.C.S.*, **53**, 1367, 3225, 1931.

THE CONSTITUTION OF THE COPPER-SILVER SERIES OF ALLOYS EXAMINED THERMODY- NAMICALLY.

BY F. H. JEFFERY.

Received 30th June, 1932.

The following describes a method of analysing the constitution of these alloys which has not been applied to them hitherto, as far as the author knows. This re-examination seems justifiable, partly because of the technical importance of some of them, and partly because of the diverse results obtained by different investigators.

The calculations are based on the equilibrium diagram given by Stockdale.¹ He found the solidus and the solid solubility curves using copper of purity 99.92 per cent. and silver of fineness at least 999.7; for the liquidus he used the results given by Heycock and Neville.

If the assumption be made that the copper-rich liquid and solid solutions consist of monatomic molecules of silver dissolved in monatomic molecules of copper the thermodynamic equation must be of the form

$$-\log (1 - n) + \log (1 - n') = \lambda/R\theta - \lambda/R\theta_0$$

where n is the molal fraction of silver in the liquid solution and n' that in the solid solution, θ_0 being the freezing-point of copper: λ is supposed to remain sensibly constant for the range of concentration and temperature examined. The results shown in Table I. were obtained:—

TABLE I.

θ .	Per Cent. Ag in Liquid.	Per Cent. Ag in Solid.	n .	n' .	$1/\theta$.	$-\log (1 - n) + \log (1 - n')$.
1356	0.0	0.0	—	—	7.375×10^{-4}	0×10^{-2}
1343	2.2	0.8	1.31×10^{-2}	0.47×10^{-2}	7.446	0.368
1333	4.4	1.4	2.64	0.83	7.502	0.800
1323	6.6	2.0	4.00	1.19	7.559	1.253
1313	8.6	2.6	5.26	1.55	7.616	1.669
1303	10.7	3.1	6.60	1.85	7.675	2.154
1293	13.0	3.7	8.10	2.21	7.734	2.697

These points lie on the straight line through the second and the sixth; this straight line should pass through the first point accurately; the first point is proximate to the line. It will be noted that the range of temperature for which λ is sensibly constant is 60 degrees. The mean value of $\lambda = 3.55 \times 10^3$.

The silver rich liquid and solid solutions were examined next, the same assumption as to the constitution being made. Using the same

¹ Stockdale, *J. Inst. Metals*, 45, 127, 1931.

notation the equation is of the same form. The results shown in Table II. were obtained :—

TABLE II.

θ .	Per Cent. Cu in Liquid.	Per Cent. Cu in Solid.	n .	n' .	z/θ .	$-\log (z-n)$ $+\log (z-n')$.
1234	0.0	0.0	—	—	8.104×10^{-4}	0.0×10^{-3}
1223	1.2	0.8	2.02×10^{-2}	1.35×10^{-2}	8.176	0.296
1213	2.3	1.4	3.84	2.35	8.244	0.668
1203	3.4	2.0	5.63	3.35	8.312	1.037
1193	4.4	2.5	7.24	4.17	8.382	1.414
1183	5.6	3.0	9.14	4.98	8.453	1.945
1173	6.8	3.4	11.01	5.63	8.525	2.548

These points lie on the straight line through the third and the sixth; this straight line is proximate to the first point but does not pass through it accurately as it should. The range of temperature for which λ is sensibly constant is again 60 degrees.

The mean value of $\lambda = 0.101 \times 10^3$.

Alike in this and in the previous case the straight lines do not pass accurately through the points given by the freezing-points of the pure metals: the author thinks that this may be due to errors in the determination of the liquidus; the liquidus was determined by means of a platinum resistance pyrometer with a heavy porcelain sheath.

If the molecular constitutions of the solutions are such as the preceding results appear to show they must be consistent with the boundary conditions given by the solid solubility curves. It is important to examine this, inasmuch as the results of various investigators differ greatly as to these curves. Calculations have, therefore, been made for intervals of 10 degrees and continued until the solutions become too concentrated to be regarded as dilute.

From the equilibrium diagram it will be seen that when a copper-rich solid solution cools from any temperature below that of the corresponding mixed phase boundary it gives rise to a copper-rich solution richer in copper than it was, and to a silver-rich solution richer in silver than the silver-rich solution in equilibrium with the original copper-rich solution at the temperature from which it cooled. One way of effecting this would be for some of the solute of the copper-rich phase to pass into the silver-rich phase, and for some of the solute of the silver-rich phase to pass into the copper-rich phase. The thermodynamic equation is

$$\nu \log n + \nu_0 \log (1 - n) + \nu' \log n' + \nu'_0 \log (1 - n') = \log K$$

where $\nu = -1$, $\nu_0 = 1$, $\nu' = -1$, $\nu'_0 = 1$

and n is the molal fraction of silver in the copper-rich phase, and n' similarly for the silver-rich phase. Also

$$\frac{\partial}{\partial \theta} \log K = \frac{-\lambda}{R\theta^2}.$$

The integration gives an equation of the form

$$-\log n + \log (1 - n) - \log n' + \log (1 - n') = \frac{\lambda}{R\theta} + \text{constant},$$

where λ is supposed to remain sensibly constant for the range of temperature and concentration examined.

The results shown in the following table were obtained :—

θ .	Per Cent. Ag in Cu Solution.	Per Cent. Cu in Ag Solution.	n .	n' .	$1/\theta$.	$-\log n$ + $\log (1-n)$ - $\log n'$ + $\log (1-n')$
893	3.0	3.9	1.79×10^{-2}	6.44×10^{-2}	1.120×10^{-3}	2.9015
903	3.2	4.2	1.93	6.92	1.107	2.8347
913	3.4	4.4	2.04	7.24	1.095	2.7890
923	3.6	4.6	2.15	7.55	1.083	2.7461
933	3.8	4.9	2.28	8.03	1.072	2.6910
943	4.0	5.1	2.40	8.33	1.060	2.6508
953	4.3	5.3	2.58	8.64	1.049	2.6013
963	4.5	5.5	2.70	8.96	1.038	2.5632
973	4.8	5.8	2.88	9.44	1.028	2.5100
983	5.0	6.1	3.01	9.91	1.017	2.4669
993	5.3	6.3	3.20	10.22	1.007	2.4245
1003	5.6	6.6	3.47	10.69	0.997	2.3662
1013	5.9	7.0	3.56	11.33	0.987	2.3264

The first eleven points lie on a straight line through the second and the eleventh; the next are proximate to this straight line but not on it; this seems to be due to the large values of n' . The value of λ remains constant for a range of at least 100 degrees.

The mean value of $\lambda = 18.7 \times 10^3$.

This confirms the previous result that the solid solutions consist of monatomic molecules of silver in copper and of copper in silver.

Summary.

The constitution of the copper-silver series of alloys is the simplest possible: the liquid solution consists of monatomic molecules of copper and of silver, the solid solutions consist of monatomic molecules of silver dissolved in monatomic molecules of copper, and of monatomic molecules of copper dissolved in monatomic molecules of silver.

*The Goldsmiths' Metallurgical Laboratory,
Cambridge.*

THE EFFECT OF OXYGEN PRESSURE ON THE CORROSION OF STEEL.

By A. R. LEE.

Received 1st July, 1932.

Previous work¹ has shown that under thermostatic conditions of complete immersion, iron and steel corrode in potassium chloride solutions under what has been described as oxygen control. By this is meant that the corrosion rate is determined by the rate of supply of

¹ Bengough, Lee and Wormwell, *Proc. Roy. Soc.*, 134A, 327, 1931.

oxygen to the metal; any specific effect which the other factors could possibly have is hidden by the limiting rate imposed by the oxygen supply; they are effective only insofar as they effect this supply. For theoretical reasons it is necessary to know if any new type of control will occur when the oxygen supply is increased. None occurs when the oxygen supply is increased by shallow immersion, wide cross-section of corrosion vessel and convection currents due to temperature variations. Hence it was decided to follow the corrosion rate at oxygen pressures above atmospheric.

A survey of the literature has shown that only three workers have hitherto attempted to measure the effect of oxygen pressure on corrosion at pressures above atmospheric. Unfortunately, their results are contradictory. Schikorr³ gives no description of experimental procedure nor details of apparatus. His specimens were iron strips 4 mm. \times 24 mm. \times 3 $\frac{1}{4}$ mm. and the loss of weight estimated after five days. His results are tabulated below:—

Oxygen pressure atms. . .	0.2	1	2	3	5
Loss of weight, mgs. . .	13.5	20.5	8	9	8

It will be noticed that corrosion rate falls to a low value above 1 atmosphere pressure.

Herzog and Chaudron³ investigated the effect of pressure of oxygen on the velocity of corrosion of duralumin in 3 per cent. NaCl for both horizontal and vertical specimens 80 mm. \times 10 mm. \times 2 mm. Their results are tabulated below:—

Oxygen pressure atms. . .	30	60	90	120	
Loss of wt. mg./m ² /day. .	54	104	165	164	Horizontal
" " " "	20	42	60	70	Vertical

With the vertical specimens they state that the top was cathodic to the bottom and also that most of the corrosion occurred at this top cathodic zone.

Chaudron⁴ published curves connecting pressure and corrosion rate of iron for vertical and horizontal specimens. Corrosion is much greater for the horizontal specimens and increases rapidly for both as the pressure is raised to about 30 atmospheres, after which the curves tend to become asymptotic to the pressure axis. The highest pressures shown were 120 atmospheres.

The contradictory results of Schikorr and Chaudron call for further work on this problem. Neither obtained corrosion-time curves.

Walker, Cederholm and Bent⁵ investigated the effect of pressure below atmospheric by using mixtures of oxygen and nitrogen. They showed that the rate of corrosion from zero pressure to one atmosphere was proportional to the oxygen partial pressure.

³ G. Schikorr, *Korr. Met.*, **4**, 242, 1928.

⁴ Herzog and Chaudron, *Comptes rendus*, **190**, 1189, 1930.

⁵ Chaudron, *Chimie et Industrie*, **26**, 277, 1931.

⁶ *J. Am. Chem. Soc.*, **29**, 1251, 1907; also **30**, 473, 1908.

Experimental Procedure.

The steel used was the standard material employed by Bengough, Lee and Wormwell in the previously mentioned work. Analysis showed the following percentages for constituents: Carbon 0.13; silicon 0.15; sulphur 0.034; phosphorus 0.034; manganese 0.46; nickel 0.20. The specimens were turned discs, 2.5 cm. diameter, 0.6 cm. thick, supported horizontally on three glass points at a depth of 1.5 cm. below the liquid-surface in a glass vessel 4.4 cm. diameter. The volume of the liquid was 100 c.c.

The weighed specimen was placed in position, and the solution which had been previously saturated with oxygen, was poured into the vessel. The vessel was then lowered into the bomb and a second similar vessel and specimen was usually placed above it, resting on the projections at the top of this vessel. The lid of the bomb was placed in position and all the joints of the system were made tight. Fig. 1 illustrates the system.

The bomb was made from a solid stainless (Firth's Staybrite) steel block, 4 ins. \times 4 ins. \times 10 ins., the end pieces being bolted on. The joint with the lid was made gas tight by an annealed copper ring which, under the pressure of the four fastening nuts, accommodates itself to the grooved shape of the joint. This

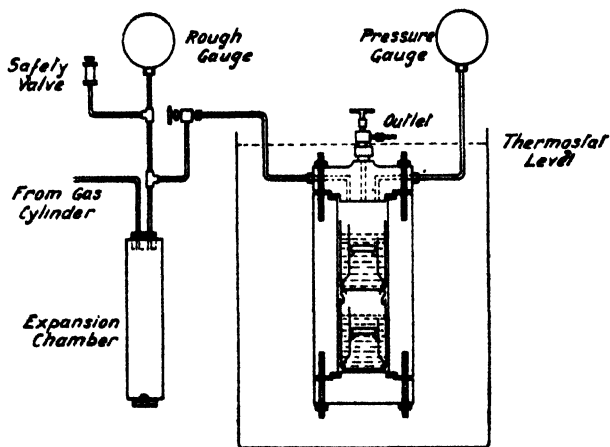


FIG. 1.

method is used for all large joints in high pressure work at the Chemical Research Laboratory. The tubing and control valves were also of stainless steel, and the gauge was a steel-tube gauge reading up to 30 atmospheres, graduated in atmospheres. The expansion chamber immediately following the supply cylinder prevented any sudden changes of pressure being communicated to the apparatus.

The bomb was permanently fixed in a water thermostat, the water from which was partly emptied when the lid was removed. The temperature was maintained at 25° C., constant to $\pm 0.02^\circ$ C.

After bolting down, the pressure in the system was raised to 10 atmospheres. The gas was then allowed to escape. This was repeated, and then the pressure was finally raised to the required value. This procedure was a simple method of reducing the original air to a very low fraction of the gas in the system; if the final pressure was 10 atmospheres the air in the system was only 1/1000th of the total gas. All the control valves were then closed.

As corrosion proceeded the fall in pressure was restored every twenty-four hours; the pressure of the experiment was taken as the mean

of the highest and lowest values. The maximum fall during any experiment rarely exceeded 1/5th atmospheres over the whole range of pressures employed.

The corrosion was estimated by loss of weight at the end of a definite time, and by using two vessels four different points could be obtained in ten days on a corrosion curve extending up to ten days. The corrosion products were loosened from the specimens by boric acid treatment, and an estimation of both the ferrous and total iron was made for each experiment. Experimental results are recorded in the table. In one experiment (3 atmospheres pressure) the gas from the bomb was taken into a modified Haldane gas analysis apparatus and tested for hydrogen. This apparatus had a 100 c.c. bulb, was fitted with a 1 c.c. burette, and indicated a change of 0.01 c.c. in the volume of the sample of gas withdrawn.

TABLE OF RESULTS.

Oxygen Pressure Atmos.	Time of Corrosion. Days.	Total Corrosion Mg.		Equiv. Oxygen Absorption c.c.	Percentage Ferrous.
		Loss of Weight.	Total Iron in Corrosion Product.		
1	Rate = 2.75 mg. per day = 0.84 c.c. per day.				
3	19	167.8	168.7	53	11.3
	38	328.3	326.5	102.9	13.6
	57	487.4	483.9	154.9	10.3
5	2	42.8	42.4	13.1	19.6
	13	70	70.1	21.6	18.6
	5	109.6	109.4	34.1	15.5
6	10	194.0	193.6	60.7	14.3
	10	257.2	255.3	81.4	10.8
	10	2	97.0	97.0	30.3
3		146.6	145.5	46.3	11.7
5		238.4	238.4	76.0	8.6
15	10	544.6	544.3	172.6	10.5
	2	153.2	154.3	48.6	10.3
	3	232.6	221.3	70.7	10.0
20	5	350.8	347.8	111.3	10.0
	10	771.6	768.6	243.9	11.1
	25	2	214.8	213.9	81.1
3		238.2	236.4	74.3	15.9
5		514.2	506.4	158.7	13.9
25	10	833.6	838.9	263.1	11.6
	2	231.2	230.3	75.8	8.4
	3	324.0	322.8	103.7	7.7
25	5	510.4	512.3	161.0	11.8
	10	875.4	878.2	273.3	14.3

A preliminary experiment with zinc in $N/10$ KCl at 1 atmosphere of oxygen was first performed in order to test the apparatus for standard results as obtained by the apparatus described in the previous work. This experiment gave a corrosion rate for thirteen days which corresponded to an oxygen absorption rate of 1.46 c.c. per day; the rate with the standard apparatus of Bengough, Stuart and Lee is 1.47 c.c.

Results.

A series of ten-day corrosion-time curves has been obtained for steel in $N/10$ KCl with a number of pressures up to 25 atmospheres. These

CORROSION-TIME CURVES

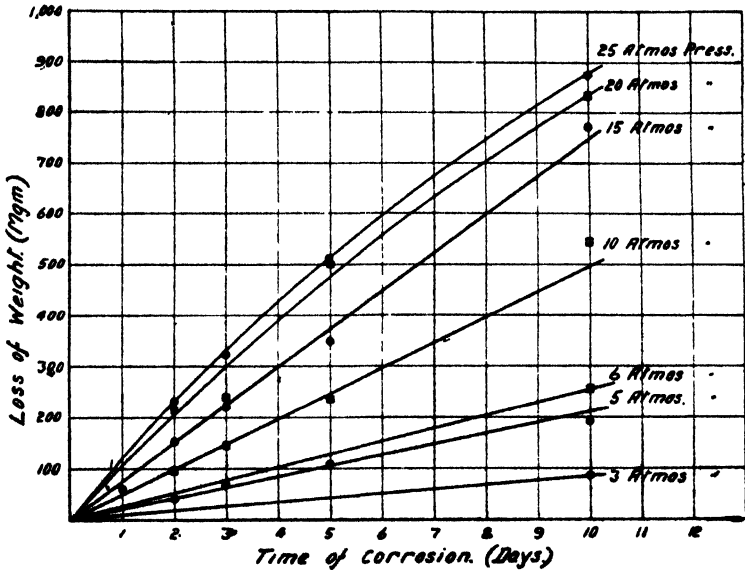


FIG 2

CALCULATED OXYGEN ABSORPTION.

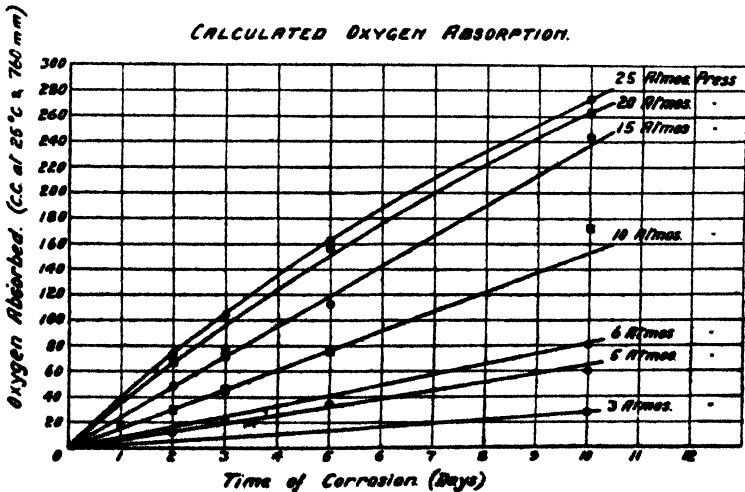


FIG. 3.

are shown in Fig. 2. Fig. 3 shows the corresponding oxygen absorption curves, which have been calculated from Fig. 2 using the experimental results of the percentage of ferrous iron in the corrosion product and neglecting any possible hydrogen evolution. It will be seen that the

corrosion-time curves are straight lines for the various pressures up to 20 atmospheres; beyond this pressure the corrosion rate falls continuously as corrosion proceeds. This change in the shape of the curve coincides with a change in the nature of the corrosion products, part of which at 25 atmospheres pressure assumes a hard granular form somewhat resembling that found in very weak chloride solutions at normal pressure. This compact material adheres to the specimen, and apparently causes a gradual diminution in the corrosion rate.

From the straight line curves of Figs. 2 and 3 the mean rates of corrosion and oxygen absorption have been calculated for the various pressures. At high pressures, where the corrosion-time curves depart from straight lines, the slopes of the tangents at the beginning have been measured. These rates are shown in Fig. 4 plotted against the

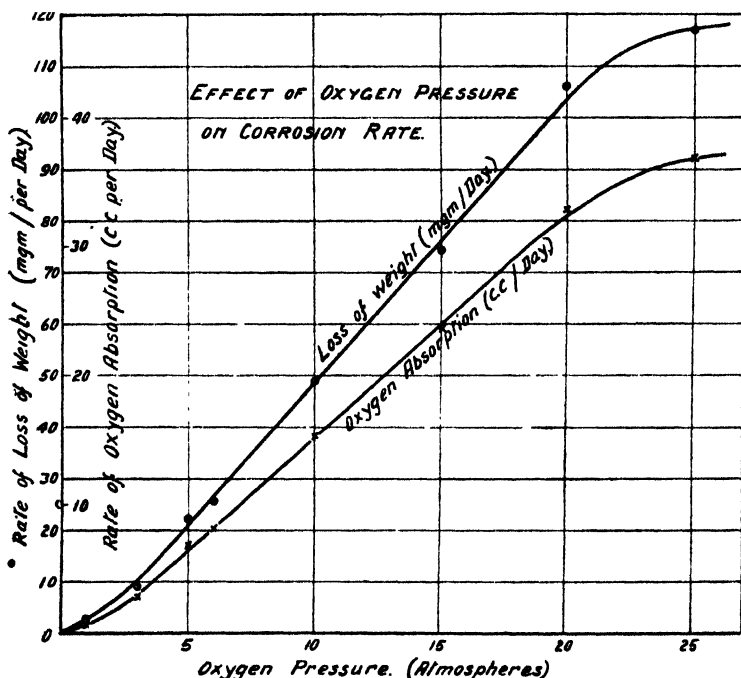


FIG 4

corresponding pressures. The curves show considerable resemblance to those of Chaudron; the chief difference is that Chaudron's curves showed appreciable corrosion at zero oxygen pressure.

It will be seen that between 1 and 5 atmospheres the curve is convex to the pressure axis, *i.e.*, for an increase in pressure the corrosion rate increases faster than does the pressure. This is perhaps one of the most interesting results of the work. Corrosion is proceeding under oxygen control and some light is thrown on this by considering the corrosion in terms of oxygen absorption. At 1 atmosphere pressure of oxygen the "characteristic" rate of absorption for $N/10$ KCl is 0.84 c.c. per day. There is no simple ratio at all between this rate and the rates at the higher pressures. However, the maximum rate at 1 atmosphere of oxygen was obtained with the very dilute chloride solutions; *e.g.*,

$N/10,000$ KCl gave a rate for the first few days of 1.5 c.c. per day. It will be seen that for pressures from 6 to 20 atmospheres the corrosion rate in $N/10$ KCl is a simple multiple of this rate and is directly proportional to the pressure, e.g., the rate at 6 atmospheres is 8.1, and at 15 atmospheres it is 23.6.

Above 20 atmospheres the curve appears to substantiate the results of Chaudron, who used pressures up to 120 atmospheres.

One experiment was performed with $N/10,000$ KCl at 6 atmospheres pressure of oxygen, the loss of weight being estimated at the end of ten days. The loss of weight was 87.6 mg. A previous set of short time loss of weight measurements showed that at 1 atmosphere pressure the corrosion in this solution after twenty-four hours was about 8.5 mg. It is obvious that in this solution there is a maximum rate of about 8.8 mg. per day which cannot be exceeded, however great the oxygen supply may be made.

The strength of the steel used for the bomb in the present work would not permit the use of pressures above 25 atmospheres.

Hydrogen.

The gas from the bomb in which two specimens had been corroding for seventeen days was passed over heated palladium black in the modified Haldane apparatus. The contraction showed that the total hydrogen in the gas was about 2.8 c.c., which corresponds to a rate of evolution per specimen of 0.08 c.c. per day. The hydrogen evolution at 1 atmosphere pressure was 0.06 c.c. per day. This is further evidence for the constancy of the hydrogen evolution previously noted with more limited variations of oxygen supply. It appears that above a small limiting rate of oxygen corrosion the hydrogen evolution rate is a function of the metal and the corroding liquid, and independent of the oxygen supply.

Distribution.

The distribution of corrosion was very similar to that produced at 1 atmosphere pressure. The corroded areas appear to spread somewhat more rapidly. The specimens at 20 atmospheres showed as much widespread corrosion as at 1 atmosphere, although the corrosion rate was about thirty times as great. Fig. 5 shows the distribution of corrosion after ten days at 5 and 20 atmospheres pressure of oxygen. It is obvious that such distribution cannot be controlled by any protective current density as described by Evans, Bannister and Britton⁶ for half immersed specimens.

Discussion of Results.

Below 20 atmospheres pressure the corrosion process is still under oxygen control, but it would appear that at higher pressures a new factor takes control. Further work is required to define this, but the results so far obtained are of use from several points of view.

Problems involving corrosion by flowing liquids are complicated by the number of variables which are introduced by the liquid movement. One of these will usually be the oxygen supply, and consequently a

⁶ *Proc. Roy. Soc.*, **131A**, 371, 1921.

study of the specific effect of fast oxygen supplies in stagnant solutions should be a preliminary to the more complicated problem. Experiments with flowing liquids have been made by Heyn and Bauer,⁷ Friend,⁸ Speller and Kendall,⁹ Evans,¹⁰ and Forrest, Roetheli and Brown.¹¹ Speller found a continual increase in the corrosion rate with increasing rates of flow. Forrest and his co-workers, however, have explained a reduction in corrosion by flowing water as due to the combined effect which liquid movement and high oxygen supplies have in producing a protective film of ferric hydroxide. The present results suggest that the effect is due rather to the movement itself, which causes the corrosion products to settle on the metal in the particular manner which these workers describe.

The results are of interest in view of statements which have been made regarding the rate of oxygen supply in passivity phenomena. With both a typical weak solution and a typical strong solution there is no evidence that a high rate of oxygen supply produces passivity or even a decrease in the corrosion rate or causes a reduction in the area of metal attacked. It would thus appear that statements which have been put forward by U. R. Evans and others¹² with reference to half immersed specimens that with oxygen pressures beyond a particular value, further increase in oxygen should diminish the corrosion rate do not apply to conditions of complete immersion. Oxygen in solution does not act as a passifier; its function appears to be simply that of a depolariser, and to some extent that of an oxidising agent for products of corrosion.

Considerable variations in oxygen pressure do not appear to affect the amount of hydrogen displaced as gas. The rate of evolution appears to be a function of the metal and of the solution, and given sufficient oxygen to allow corrosion to proceed at all, large variations in the oxygen supply may be made without affecting the hydrogen rate. Cf. previous statement of Bengough, Lee and Wormwell.

It is suggested that the results of this research might form the basis of an acceleration test. At 20 atmospheres the corrosion at the end of ten days (840 mg.) would require over 300 days at 1 atmosphere of oxygen, and over four years with air. In designing an accelerated corrosion test it is necessary to define the factor controlling the corrosion rate under normal conditions. This factor may then be modified so as to increase the rate, but it must not be intensified to such an extent that a new factor takes control. This limitation holds with oxygen pressures up to 20 atmospheres for the experiments described.

Summary.

A series of corrosion time curves for steel in $N/10$ KCl has been obtained for oxygen pressures from 1 to 25 atmospheres at 25° C.

For pressures of 1 to 20 atmospheres these are straight lines; above 20 atmospheres the corrosion rate diminishes with time.

⁷ *Mitt. Kön. Materialprüf.*, 93, 1910.

⁸ *Iron and Steel Inst. (Car. Sch. Mem.)*, 11, 128, 1922.

⁹ Speller and Kendall, *Ind. Eng. Chem.*, 15, 134, 1923.

¹⁰ *Corrosion of Metals*, 108, 1926.

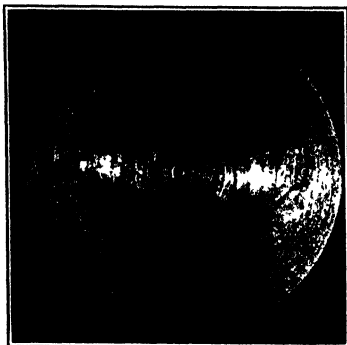
¹¹ *Ind. Eng. Chem.*, 22, 1197, 1930; also 23, 350, 1931.

¹² *Journ. Franklin Inst.*, 208, No. 1, 55, 1929; *Proc. Roy. Soc.*, 131A, 373, 1931; *Journ. Inst. Metals*, 1931, No. 2, 18. See results of Chaudron for vertical specimens.

10 days at 5 atmospheres pressure.

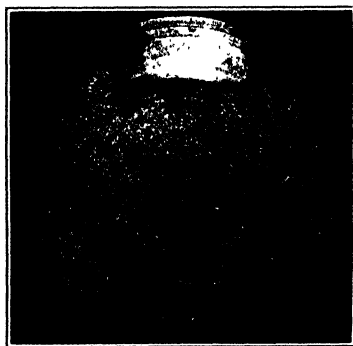


Top.



Bottom.

10 days at 20 atmospheres pressure.



Top.



Bottom.

FIG. 5.

To face page 714.

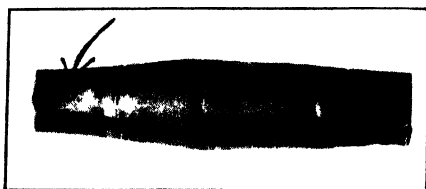


FIG. 3. Fractured nitrided fatigue specimen. The arrow shows the apparent flaking, which is really due to tearing of the case after the core had cracked.

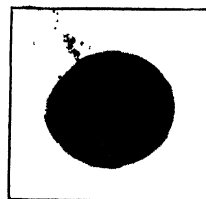
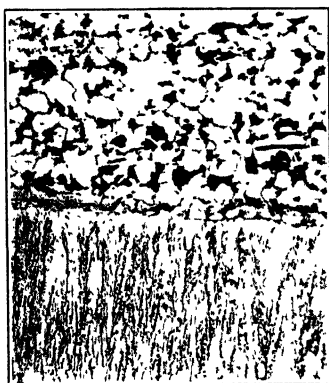


FIG. 4. Fatigue fracture of nitrided specimen. Note that failure has commenced in the core material immediately below the case.



(300)

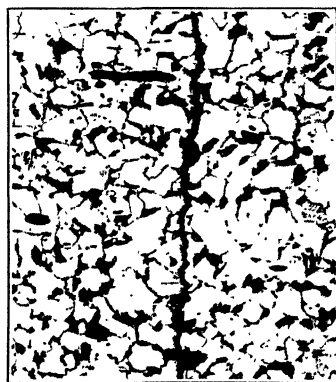


(300)

Nickel-plated Specimens.

FIG. 5.- Showing the junction between the mild steel and the nickel.

FIG. 6. Crack which commenced in the plating and continues through the steel. In this case the crack occurred at a distance from the point of maximum stress.



(500)

FIG. 7. This is the continuation of the crack shown in Fig. 6. The transcrystalline nature of the crack is typical of fatigue failure.

[See page 720.

The corrosion rate increases with increase of oxygen pressure. From 1 to 5 atmospheres the increase is greater than the corresponding pressure increase; from 5 to 20 atmospheres the corrosion rate is proportional to the pressure; above 20 atmospheres the corrosion rate appears to tend to a constant limiting value.

With $N/10,000$ KCl the maximum rate at 1 atmosphere is not increased by raising the oxygen pressure.

There is no evidence that passivity is produced by oxygen at high pressures.

It is suggested that oxygen pressures might be used for an accelerated corrosion test; the corrosion produced after ten days at 20 atmospheres pressure would require over four years with air.

The author wishes to acknowledge the help given by Mr. T. J. Nurse with the experimental work, and by Mr. Tongue and workshop staff in the design and construction of the pressure apparatus, also to express appreciation of the interest shown by Dr. G. D. Bengough. This research has been carried out for the Corrosion of Metals Research Committee of the Department of Scientific and Industrial Research, and the thanks of the author are due to Professor Sir Harold Carpenter and to Professor G. T. Morgan for facilities afforded and for permission to publish.

CORROSION-FATIGUE TESTS OF NITRIDED STEEL AND NICKEL-PLATED STEEL IN RIVER TEES WATER.

By N. P. INGLIS, PH.D.M.ENG., AND G. F. LAKE, M.A.

Received 7th July, 1932.

It has been shown in a previous paper¹ by the authors that the simultaneous action of River Tees water and alternating stress is of exceptional severity and that the "corrosion-fatigue limit" of mild steel in Tees water is certainly not greater than ± 2 tons/sq. in. The investigation described in the above paper was undertaken owing to the failure of mild steel pump shafts at the works of I.C.I. (Fertilizer and Synthetic Products), Ltd., Billingham-on-Tees. These pump shafts were subjected to the action of River Tees water and the investigation showed the reason for these failures and also showed that a Chromium-Nickel Austenitic steel would be satisfactory under similar conditions. As a result of this investigation, shafts made of 18/8/1 Chromium-Nickel-Tungsten steel were fitted in these pumps and these have given satisfactory service during the past year. However, it was decided to continue the research chiefly to determine whether certain other materials would be equally suitable.

The materials selected for test were nitrided chromium-aluminium-molybdenum steel (known commercially as "Nitalloy"), and nickel-plated mild steel. Later, as a result of the tests on the nitrided steel, cyanide-hardened mild steel was also tested, although these latter tests are still in a comparatively early stage.

¹ *Trans. Far. Soc.*, **27**, 803, 1931.

Methods of Testing.

The fatigue testing machines used were fully described in the authors' previous paper, and it is here sufficient to state that the machines were of the rotating beam type of similar design to those used in the Fatigue of Metals Laboratory at the University of Illinois.² For the corrosion-fatigue tests a steady drip of a few drops per second of River Tees water was allowed to fall on the centre of the rotating test piece. The supplies of river water for the tests were always taken at high tide from the same spot (about six miles from the mouth of the Tees). A typical analysis of the water is as follows:—

Total solids	2954	} per 100,000 parts.
Lime	48	
Magnesia	164	
SO ₂	176	
Fe ₂ O ₃ and Al ₂ O ₃	0.4	
Chlorine (as Cl)	1441.0	

Tests Carried Out.

The following fatigue and corrosion-fatigue tests have been carried out:—

- (1) Corrosion-fatigue tests of nitrided chromium-aluminium-molybdenum steel and of the same steel in its original (un-nitrided) condition in River Tees water.
- (2) Fatigue tests in air of mild steel nickel-plated with a nickel deposit 0.02 inches thick.
- (3) Corrosion-fatigue tests in River Tees water of the above nickel-plated steel.
- (4) Corrosion-fatigue tests in River Tees water of cyanide treated mild steel.

All the tests were carried out at room temperature.

Materials.

(a) **Nickel-plated.**—The nickel-plated specimens were cut from good quality mild steel bar, which was of about 0.20 per cent. carbon content, and was carefully normalised before cutting the specimens. The specimens were machined and were then sent to a firm, specialising in the deposition of metals, for nickel-plating. The thickness of nickel deposited was 0.02 inches.

(b) **Nitrided Steel.**—The "Nitalloy" steel used for nitriding had the following composition:—

Chromium	1.58 per cent.
Aluminium	0.87 "
Molybdenum	0.33 "
Carbon	0.26 "

This was supplied by Dr. Hatfield, of the Brown-Firth Research Laboratories, who also carried out the nitriding after the specimens had been machined. (The authors' best thanks are due to Dr. Hatfield for his kindness in this matter.) The above steel was supplied in the hardened and tempered condition, and after the specimens had been rough machined they were all given a treatment at 550° C. in order to relieve all machining

² Univ. of Illinois Engineering Expt. Station Bulletin No. 152.

stresses at this stage rather than in the subsequent nitriding operation. As is well known, the nitriding process consists in heating the special chromium-aluminium-molybdenum steel in an atmosphere of ammonia at a temperature of 500° C. The time of heating in the ammonia atmosphere to produce a case 0.015 inches deep is about 90 hours. The "Nitalloy" steel which was tested in the un-nitrided condition was given exactly the same heat treatment as that which was nitrided.

(c) **Cyanide-hardened Steel.**—A certain number of tests are being carried out on cyanide-hardened mild steel, but these are at present in an early stage. Details of the cyaniding treatment are given later in this paper.

Test Results.

The test results are given in Tables I. and II., and these results are plotted as "Stress-reversals curves" in Figs. 1 and 2. The ordinary

TABLE I.—FATIGUE TESTS ON NICKEL-COATED MILD STEEL (0.02-INCH NICKEL DEPOSIT).

Conditions of Test.	Range of Stress Tons/in. ²	Reversals to Fracture.	Remarks.
In air.	± 21.3 ± 17.1 ± 12.7 ± 11.2 Estimated fatigue limit ± 11.2 tons/in. ²	22,550 133,750 805,350 13,050,000	Broken. " " Unbroken.
Subjected to drip of River Tees water.	± 12.3 ± 10.1 ± 7.4 ± 5.9 ± 4.7 ± 3.7 Estimated corrosion-fatigue limit less than ± 3 tons/in. ²	740,250 1,772,400 9,074,600 44,535,350 35,388,150 170,417,600	Broken. " " " " "

TABLE II.—FATIGUE TESTS ON "NITRALLOY" STEEL, NITRIDED AND UN-NITRIDED.

Conditions of Test.	Range of Stress Tons/in. ²	Reversals to Fracture.	Remarks.
Nitrided : in air ^a	Estimated fatigue limit ± 37 tons/in. ²		
Un-nitrided : in air ^a .	" "	" ± 33 tons/in. ²	
Nitrided : subject to river water drip.	± 40.5 ± 35.4 ± 30.1 ± 27.9 ± 24.8 Estimated corrosion-fatigue limit ± 25 tons/in. ²	177,900 477,050 1,930,400 6,486,500 101,000,000	Broken. " " Unbroken.
Un-nitrided : sub- ject to river water drip.	± 29.7 ± 22.0 ± 12.2 ± 9.3 ± 7.4 ± 5.4 Estimated corrosion-fatigue limit less than ± 5 tons/in. ²	77,300 166,150 2,678,850 18,312,650 8,736,150 11,320,350	Broken. " " " "

air-fatigue limits for the "Nitr alloy" steel, nitrated and unnitrated, are taken from a paper by N. L. Mochel,³ and his results are substantially confirmed in a recent paper by Dr. A. Fry.⁴

The chief results of the present tests are briefly summarised in Table III. below.

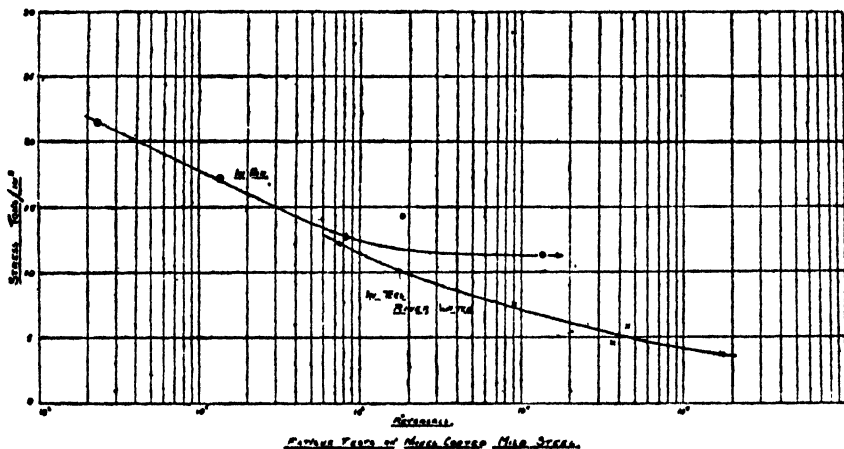


FIG. 1

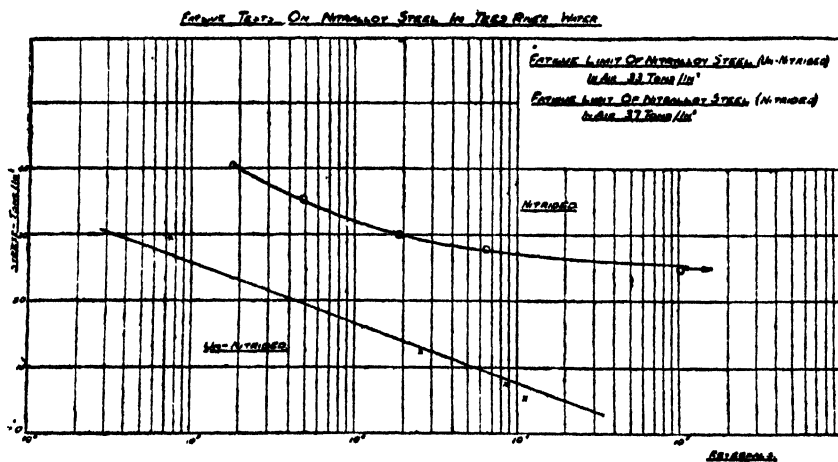


FIG. 2

Considering the results on the nickel-coated steel, it will be seen from Fig. 1 that the presence of the nickel deposit has considerably reduced the ordinary air-fatigue limit as compared with that of the original mild steel. It is believed that the reason for this big reduction in the fatigue limit is due to internal stress in the coating, and the microscopic examination described later offers some confirmation of this. This particular effect was studied in detail by Barklie and Davies,⁵ who showed

³ American Soc. for Testing Materials, Vol. 30, Part II.

⁴ Iron and Steel Inst., 1932, also Engineering, May 13th, 1932.

⁵ Proc. Inst. Mech. Engrs., May, 1930.

that the internal stress in the nickel deposit acted as an added steady stress and so altered the applied fatigue range. They further showed that once a crack had started in the nickel deposit it was readily propagated through the steel, and this was also found to be the case in the present tests. This result is of considerable importance, particularly since worn parts of shafts, etc., are frequently built up to their original dimensions by depositing nickel, and, if such parts are to be used under fatigue conditions, the method of depositing must be critically examined to ensure that the internal stress in the deposit is kept down to a minimum. The corrosion-fatigue results obtained from the nickel-coated specimens are very disappointing. Although tests have been carried to 170,000,000 reversals, a definite fatigue limit has not been determined, but, if one exists, it is certainly not more than ± 3 tons/sq. in. While this is superior to ordinary mild steel the improvement effected by the nickel deposit is not sufficiently great to justify the use of nickel-plated material under these particular corrosion-fatigue conditions.

TABLE III.

Material.	Fatigue Limit in Air. Tons/Sq. In.	Corrosion-fatigue Limit in Tees River Water. Tons/Sq. In.
Mild steel.	± 17.0	Less than $\pm 2.*$
Mild steel, nickel-plated.	± 11.2	Not more than ± 3.0 .
"Nitalloy" steel, not nitrided.	± 33.0	Less than ± 5.0 .
"Nitalloy" steel, nitrided.	± 37.0	± 25.0
18/8/1 Cr. Ni. W. steel, fully softened.	$\pm 17.6 *$	$\pm 11.1 *$
18/8/1 Cr. Ni. W. air-cooled from 650° C.	$\pm 17.6 *$	$\pm 6.5 *$

* The results of the previous tests are included in this summary for ease of reference (see *Trans. Faraday Soc.*, **27**, 803, 1931).

It should be noted that, in one or two of the nickel-plated specimens, cracks actually developed in parts of the specimen not under the maximum applied stress, although in all cases the final fracture occurred at the point of maximum stress.

The results given by the nitrided material are of extreme interest and importance. It will be seen that the nitrided steel has a corrosion-fatigue limit of ± 25 tons/sq. in. and that this value is much higher than that given by 18/8/1 Chromium-Nickel-Tungsten steel under the same conditions. In addition, the ratio $\frac{\text{corrosion-fatigue limit}}{\text{air-fatigue limit}}$ is 0.67 for the nitrided material and 0.63 for the Chromium-Nickel Austenitic steel. The results also make it quite clear that the excellent corrosion-fatigue properties of the nitrided steel are due to the nitrided case and are not due to any inherent virtue of the special chromium-aluminium-molybdenum steel, since tests on this steel in the un-nitrided condition gave a corrosion-fatigue limit of less than ± 5 tons/sq. in.

In view of the good results given by the nitrided steel it was decided to try the effect of cyanide-hardening of mild steel, since such cyanide treatment is both a carburising and nitriding operation. The experiments on cyanide-hardened steel are still in progress, but the following results obtained up to the present, are extremely promising:—

Specimen No.	Range of Stress.	Reversals to Fracture.
1	± 24.5	416,000
2	± 19.5	13,047,600
3	± 16.9	24,797,400
4	± 14.8	43,237,650
5	± 12.5	70,000,000 unbroken

All of the above specimens were tested under corrosion-fatigue conditions, so that there is a definite indication that excellent corrosion-fatigue resistance can be obtained from cyanide treated mild steel. The actual treatment given to the mild steel was to heat at 900° C. for 4 hours in a bath containing 50 per cent. sodium-cyanide and 50 per cent. soda ash. After this treatment the specimens received a double quench, first a quench in oil from 890° C. followed by a quench in water from 780° C. The specimens were then ground to the finished diameter (0.375 inches), and it was found that the above treatment had produced a case of 0.10 inches. The ratio of $\frac{\text{case}}{\text{diameter}}$ is therefore extremely high and it will be necessary later to test case thicknesses more in accordance with the usual practice. It will be noted, however, that even with this heavy case the stress in the mild steel below the case in specimen No. 5 (above) is very much greater than the corrosion-fatigue limit of mild steel.

Examination of Fractures.

The type of fracture of the nitrided specimens under fatigue is rather peculiar and at first sight gives the impression that the nitrided case has flaked off. Fig. 3 is a photograph of a broken nitrided fatigue specimen and the apparent flaking is indicated by the arrow head. Fig. 4 shows the actual fracture in service of this particular specimen, and it will be noted that the fatigue failure has commenced in the *core material* immediately below the case. This shows very clearly that the core has cracked due to fatigue and that the cracking of the core has finally caused tearing of the case, *i.e.* the nitrided case never failed by fatigue but cracked away after the core had cracked. This explains the apparent flaking of the case. A similar type of failure is shown in Dr. Fry's recent paper.⁴

Microscopic examination of the nickel-coated specimens showed that the deposit was uniform in thickness and was free from porosity. The usual test for porosity with paper soaked in potassium ferricyanide showed excellent soundness. The adhesion between the nickel and the mild steel was exceptionally good. Fig. 5 is a microphotograph showing the junction of the mild steel and the nickel, and the long columnar crystals of the nickel will be noted and are typical of chill cast material, or of crystals gradually growing on a comparatively cold surface. It can be readily appreciated that such a coating is in a state of considerable internal stress, and the fact that the ordinary fatigue limit of this material is much below that of the mild steel is a further indication of this. As pointed out by Barklie and Davies, nickel can be deposited with very little internal stress and it is clearly necessary to obtain this condition for resistance to fatigue. It would be interesting to investigate the possibility of improving the fatigue properties of nickel-plated steel by a stress-relieving heat treatment after depositing.

Fig. 6 shows the crack which occurred on the nickel-plated specimen some distance from the final fracture, at a place where the applied stress was somewhat less than 90 per cent. of the maximum stress. Obviously there must have been some source of weakness at this point and the cracking is either due to high internal stress in the deposit, which would increase the range of stress, or else to porosity in the coating which allowed the river water to get through and act on the mild steel. As both microscopic examination and the ferricyanide test showed excellent soundness, it must be concluded that internal stress in the plating is responsible for this cracking. Apparently once a crack has started in the plating it can be propagated through the mild steel, due to stress concentration at the root of the crack, in much the same way as a surface crack in a piece of steel is propagated through a tough and ductile core. The crack in the nickel-plating shown in Fig. 6 continues through the mild steel in the manner shown in Fig. 7, and it will be noted that the crack in the mild steel is a typical transcrystalline fatigue crack, although this particular test piece failed under corrosion-fatigue conditions.

The writers wish to thank the directors of I.C.I. (Fertilizer and Synthetic Products), Ltd. for permission to publish this paper.

ABSORPTION AND CLASSICAL DIFFUSION.

By A. T. MCKAY, M.Sc.,
of the British Boot, Shoe and Allied Trades Research Association.

Received 13th July, 1932.

The purpose of this paper is to discuss certain aspects of the phenomena of absorption in relation to the classical diffusion mechanism.

A perusal of the literature reveals that many workers¹ have postulated or attempted to deduce, on theoretical grounds, that the process of absorption is governed, at least in a statistical sense, by the Fick diffusion law, and they have sought to confirm their view by the examination of experimental data. We make it, therefore, one of our first points to look a little more closely into the methods of analysis which have been employed with observational material. The procedure generally adopted by most workers is as follows:

The Fick partial differential diffusion equation applicable to the infinite plane sheet

$$\frac{\partial^2 \theta}{\partial x^2} = \frac{I}{k} \frac{\partial \theta}{\partial t} \quad . \quad . \quad . \quad . \quad (I)$$

is assumed, and a solution is formally derived by using some set (one of many alternatives !) of apparently suitable boundary conditions which,

¹ J. W. McBain, *Z. physik. Chem.*, **68**, 471, 1909. J. W. McBain, *Trans. Far. Soc.*, **14**, 202, 1919. A. F. H. Ward, *Proc. Roy. Soc.*, **133A**, 522, 1931. L. Friedmann and O. Kraemer, *J.A.C.S.*, **52**, 1295, 1930. H. Bradley, A. T. McKay and B. Worswick, *J.I.S.L.T.C.*, **13**, 1929. D. H. Andrews and I. Johnstone, *J.A.C.S.*, **46**, 9, 1924.

40, 9, 1924.
 "The Adsorption of Gases by Solids." A general discussion held by the Faraday Society, 1931. (This will be referred to in the text as the "Discussion.")

by analogy with heat problems, appear appropriate to the particular experimental conditions in question. By an integration across the thickness of the sheet a quantity-time relation of the form

$$Q = Q_m f(kt/a^2) \quad . \quad . \quad . \quad (2)$$

is derived. The next step is then to test if the experimental data can be adequately represented (*i.e.* to within the degree of experimental error) by equation (2), provided the numerical values of the parameters are suitably chosen. To do this the general practice seems to proceed in one or other of the following ways:—

1. The numerical ³ value of $f(x)$ is computed for a range of values of x and possibly a large scale graph of the function is constructed. The asymptotic value of Q being known on *theoretical grounds*, the values of x corresponding to each observed value of Q/Q_m are found therefrom. If these values are closely constant (*i.e.* show no definite trend) the hypothesis is regarded as confirmed, and the mean value of x/t is taken as the "best" value of the parameter.

2. An approximation ³ to f is sought for small values of kt/a^2 . In nearly all cases met with this proves to be

$$Q = AQ_m(kt/a^2)^{\frac{1}{2}} \quad . \quad . \quad . \quad (3)$$

where A is generally a mere number. The "test" of experimental data then consists in showing the approximate constancy of the ratio $Q/t^{\frac{1}{2}}$ and possibly also the constancy of Q/Q_m for a fixed t and varying external conditions.

3. A ⁴ special case of the diffusion equation is assumed *viz.*: the monomolecular reaction equation. This may be derived by making $k \rightarrow \infty$ in the case (A) which we are to consider later in the theoretical section. The resulting equation in our symbols is

$$Q = Q_m(1 - e^{-ct/2a^2}) \quad . \quad . \quad . \quad (4)$$

The test of data is obviously made by enquiring if the ratio $(1/t) \log(1 - Q/Q_m)$ is approximately constant.

4. An approximation ⁵ to f is found for large value of kt/a^2 . This usually proves to be of the form

$$Q = Q_m(1 - \alpha e^{-\beta kt/a^2}) \quad . \quad . \quad . \quad (5)$$

by neglecting all but the highest powered exponential term. The constants α and β are generally functions of π .

5. The absorption curve ⁶ is supposed exponentially asymptotic when t is large. The observational readings being supposed taken at equidistant intervals of time values of the ratio $(\Delta EQ_t)/(\Delta Q_t)$ are found from several of the late points (the notation is the usual one of the calculus of finite differences). It will generally be found that these ratios are closely constant. The mean value is then found and equated to $e^{-\lambda \cdot \Delta t}$, thus a numerical value of λ is readily determined. It will be noted, in contradistinction to the four previous methods, this one does not require that we should know, find or guess a value of Q_m . The

³ Friedmann and Kraemer, *loc. cit.*

⁴ A. F. H. Ward, *loc. cit.* Dunn, *Proc. Roy. Soc.*, 111A, 210, 1926.

⁵ H. Freundlich, *Colloid and Capillary Chemistry*, p. 696 (Methuen, 1926).

⁶ McBain, *loc. cit.* Andrews and Johnstone, *loc. cit.*

^{*} This hitherto unpublished method is used in the laboratories of the Boot Trade Research Association.

observed values of Q are then plotted against the simple diffusion ⁷ function $\psi(\lambda)$ and generally a very good straight line results. It does not, however, always pass through the origin, and we are therefore obliged to assume the fitting equation as

$$Q = Q_i + (Q_m - Q_i) \psi(\lambda) \quad . \quad . \quad . \quad (6)$$

This leads to the view that while the simple diffusion hypothesis is supposed acceptable, there must be included a constant term which is due to disturbing factors at the start of the experiment.

Having now reviewed the various methods that are in use for the purpose of testing the diffusion hypothesis, we shall consider two forms of the function f . Amongst other things, we shall try to show that the foregoing methods are insufficient to confirm the diffusion mechanism, unless special care is taken in collecting the data and the particular fitting curve is first carefully analysed.

Theoretical.

Consider the formal solution of the following problem :—

An infinite plane sheet of absorbent material has its faces in the presence of absorbates of the same intensities. Supposing that the absorption process is expressed by the usual partial differential diffusion equation, together with boundary conditions involving a surface conductivity, it is required to find an expression for the quantity of absorbate absorbed in any time interval. It will be supposed that the concentration of any element of the material is a linear function of the external concentration that would be in equilibrium with it.

Symbols.—Let the suffix 1 refer to the region *outside* the sheet.

t	time.
x	perpendicular distance from the mid-plane.
θ	concentration at plane x at time t .
Q	$2a, \theta$.
θ_1	external concentration.
Q_1	$2a \cdot \theta_1$.
θ_a	concentration <i>just within</i> the planes $x = \pm a$.
Q_m	asymptotic value of Q .
a	half the thickness of the sheet.
c	surface conductivity.
k	diffusivity constant.
γ	$2k/c$.
q^2	$\frac{1}{k} \frac{d}{dt}$.

Before the diffusion equation

$$\frac{\partial^2 \theta}{\partial x^2} = q^2 \theta \quad . \quad . \quad . \quad . \quad . \quad (7)$$

can be solved it is, of course, necessary to know what physical conditions are assumed operative at the faces of the sheet. Guided by the nature of the experimental conditions of the data under review in the last section, the following end conditions have been selected :—

⁷ $\psi(x) = \{1 - 8/\pi^2(e^{-x} + 1/9e^{-9x} + 1/25e^{-25x} + \dots)\}$ has been named "The Simple Diffusion Function," and tabulated by the present author in *Proc. Physic. Soc.*, 42, 235, 1930.

Generally speaking, a formal expansion of a function of p and interpreting by the above formula leads to either a convergent or asymptotic series in integral or fractional powers of x . Let us consider the operator $1/(p^{\frac{1}{2}} + h)$ where h is a constant. Expanding formally in ascending powers of $1/p^{\frac{1}{2}}$ and interpreting each term of the series we easily find

$$\frac{1}{p^{\frac{1}{2}} + h} = \frac{1}{h} \left\{ 2h \sqrt{\frac{x}{\pi}} - \frac{h^2 x}{1!} + \frac{2 \cdot 2}{1 \cdot 3} \frac{(h \sqrt{x})^3}{\sqrt{\pi}} - \frac{h^4 x^2}{2!} + \dots \right\} \quad (13)$$

$$= \frac{(1 - e^{h^2 x})}{h} + 2 \sqrt{\frac{x}{\pi}} \left\{ 1 + \frac{2xh^2}{1 \cdot 3} + \frac{(2xh^2)^2}{1 \cdot 3 \cdot 5} + \dots \right\} \quad (14)$$

which are convergent series since the bracketed series in (14) has each of its terms respectively less than the terms of the expansion of e^{2xh^2} . Again, expanding the operator as an ascending series in $p^{\frac{1}{2}}$ we find

$$\frac{1}{p^{\frac{1}{2}} + h} = \frac{1}{h} \left\{ 1 - \frac{x^{-\frac{1}{2}}}{h \sqrt{\pi}} + \frac{2x^{-\frac{3}{2}}}{h^3 \sqrt{\pi}} - \dots \right\} \quad (15)$$

which is an asymptotic series in which the error in stopping at any term is less than the succeeding term.

Further, we note that $p^{\frac{1}{2}}$ can be regarded as of the order $1/(\pi x)^{\frac{1}{2}}$ for the purposes of approximation. We have now before us all that is required for our present purposes.

Let us return to equation (10). First, make k approach $\rightarrow \infty$ then we have

$$Q = \frac{Q_1}{\left(\frac{2a^2}{c} p + 1\right)} = Q_1 \{1 - e^{-ct/2a^2}\}. \quad (16)$$

which is, of course, equivalent to the monomolecular law.¹² Again, we can rewrite equation (10) in the form

$$Q = Q_1 \frac{\tanh qa}{qa} / (1 + \gamma qa \tanh qa) \quad (17)$$

and when $c \rightarrow \infty$ this reduces to

$$Q = Q_1 \frac{\tanh qa}{qa} = Q_1 \psi(\pi^2 kl/4a^2) \quad (18)$$

where ψ is the simple diffusion function already mentioned in a previous footnote. The case to which (18) corresponds is that which seems to have been considered by nearly all the workers who have approached the problem from Fick's equation.¹³ The equation (18) is also an approximation to the general case when $c\pi l/a^2$ is very large compared with unity for (17) can be expanded in the form

$$Q = Q_1 \frac{\tanh qa}{qa} \{1 - \gamma qa \tanh qa + \dots\} \quad (19)$$

Thus we conclude that when t is large enough the absorption approximately follows the simple diffusion law.

We shall now consider what we can learn from equations (10) and (11) by supposing $e^{-a/\sqrt{h\pi t}}$ small compared with unity. In this case the coth and tanh terms can be written unity, and we then find:

Case (A).

$$Q = Q_1 \left\{ \frac{1}{qa} - \frac{1}{qa + 1/\gamma} \right\} \quad (20)$$

¹² Freundlich, *loc. cit.*, p. 695.

¹³ See footnote 1.

Case (B)

$$Q = Q_1 \left\{ \frac{1}{qa} - \frac{1}{qa + c} \right\} \quad . \quad . \quad . \quad (21)$$

provided that kt/a^2 is less than some quantity we shall call τ . It is thus immediately apparent that for $0 \leq kt/a^2 < \tau$ cases (A) and (B) *have the same approximate functional form*. This fact is obviously very important for it suggests that there may be many, if not an indefinite number of cases, which, arising from very different boundary conditions, yield the same approximate relationship between Q and t for some considerable time after the start. We conclude therefore that the consideration of data from the early stages of the experiment cannot possibly enable us to affirm that any particular set of boundary conditions are the only ones that could be consistent with the experimental conditions.

The study of case (B) has now been carried far enough for our purposes, and from now on we shall discard it and concentrate our attention on case (A) which seems to have greater possibilities in connection with the class of data with which we have to deal.

From equation (20) with the aid of (13) we see that a first approximation to Q is given by

$$Q = Q_1 ct/a \quad . \quad . \quad . \quad . \quad (22)$$

which will hold when t is sufficiently small. Again, using (14) we find that for medium values of t the following can be an approximation:

$$Q = Q_1((4tk/\pi a^2)^{1/2} - 2k/c) \quad . \quad . \quad . \quad (23)$$

The facts that we have deduced concerning the relation between Q and t for case (A) can therefore be summed up as follows:

- (1) When t is small Q is proportional to t .
- (2) When t is moderate Q is a linear function in $t^{1/2}$.
- (3) When t is large Q is proportional to $\psi(\pi^2 kt/a^2)$.
- (4) When c is very small the proportionality to t persists for a much longer time than when c is large.
- (5) On the other hand, when c is very large the curve has a very large initial slope, which curves into parabolic form.

We conclude this section by recording the chief sources of difficulty which arise in attempting to confirm with a reasonable degree of probability whether data can be adequately represented as arising from a diffusion law:

(I) There is possibly an initial adsorption¹⁴ which takes place instantaneously at the start so that $Q > 0$ when $t = 0$.

(II) The collecting of experimental data presents many practical difficulties which make it almost impossible to carry on the experiments, *under uniform conditions*, long enough to get a reliable value of the saturation absorption. Thus those methods of analysing data which depend upon the use of Q_m cannot prove of much assistance.

(III) The theoretical $Q-t$ relations derived from the diffusion equation generally consist of an infinite series of exponential terms from which it is next to impossible to find directly numerical values of the parameters to provide the "best fit" to the data.

(IV) The theoretical $Q-t$ curves derived by assuming widely different boundary conditions do not, in general, show any striking difference in shape from each other or from a simple exponential curve.

¹⁴ E. K. Rideal, *Discussion*, p. 144; A. F. H. Ward, *Discussion*, p. 402.

Thus, many of them start from zero, proceed for a time linearly in t , then later proceed linearly in $t^{\frac{1}{2}}$ and finally approach their asymptote exponentially. It is therefore very difficult to distinguish one from the other, unless the entire "run" of the curves are well in evidence.

Experimental.

The experiments within our purview consist in bringing a thin sheet of the specimen into contact with an absorbate of definite intensity and periodically determining the amount absorbed. From the study of a large number of cases it has been suggested that, in general, the absorption can be divided into parts:

1. An almost instantaneous *adsorption* and/or capillarity gain.
2. A slow absorption to an asymptotic value.

It is one of the main purposes of the present work to enquire to what extent the case (A) already derived can represent the slow absorption process mentioned above. It may be pointed out that in no case was it possible to obtain sufficient experimental data to fit by the method of moments put forward in the *Proc. Physic. Soc.*¹⁵ This deficiency of experimental points is, however, an inherent difficulty in nearly all questions in connection with absorption, and it therefore becomes a definite problem to make deductions in spite of it. We may note in passing a point which should be attended to in future experiments of the kind herein contemplated:

In the early stages of the absorption the readings should be taken at consecutive equal intervals of $t^{\frac{1}{2}}$ while towards the end of the absorption the readings should be taken at consecutive equal intervals of t . If this be done it becomes an easy matter to test the early and late approximations by taking differences.

We shall now consider some actual experimental data collected from various sources.

Case (I.) The Absorption of Water by Fibre Boards.¹⁶

In Fig. 1 are shown the plottings of Q against $t^{\frac{1}{2}}$ for a number of fibre boards. Considering that the experimental error can be of the order of about 3 per cent. the linearity of these curves can be regarded as excellent. Let us consider, for example, No. 4 in the following Table I:—

TABLE I.

t .	Q (obs.).	Q_0 (calc.).	$Q - Q_0$.
0.25	5.71	5.76	- 0.05
0.50	7.88	7.89	- 0.01
1.00	11.10	10.96	+ 0.14
2.00	15.15	15.27	- 0.12
4.00	21.45	21.41	+ 0.04
7.00	27.00	—	—
24.00	37.15	—	—

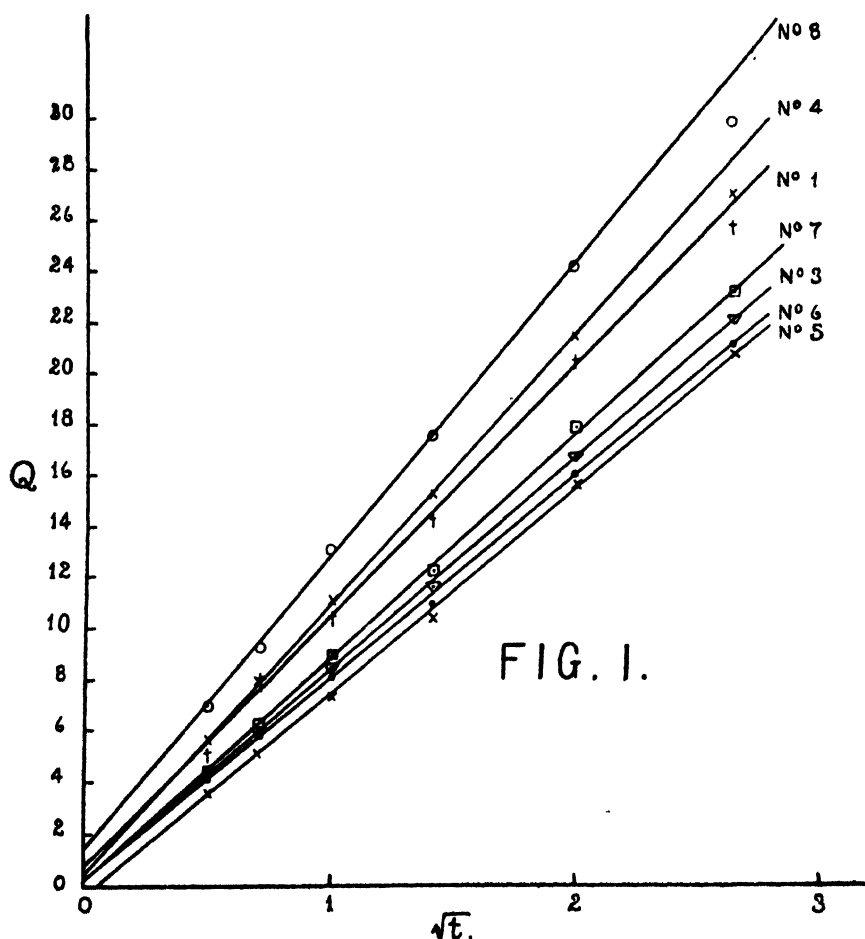
¹⁵ *Loc. cit.*

¹⁶ From the records of the Boot Trade Research Association.

The value of Q_0 in the third column has been calculated from the equation

$$Q_0 = 0.509 + 10.45 \sqrt{t}.$$

The maximum error is thus about 1.4 per cent. which is well within the experimental error. The remaining curves of figure give much the same kind of results, and we can therefore conclude that in the early stages the absorption of water by fibre boards follows a \sqrt{t} form. Owing to the lack of data nothing can be said about the late stages of the absorption.



Case (II). The Absorption of Water by Waxed Upper Leather.¹⁷

In Fig. 2 are shown the plottings of Q against t for a number of Waxed Upper Leathers. Let us select Nos. 2 and 10.

The values in the second and fifth columns are observed, while those in the third and sixth columns are calculated from

No. 2	:	:	:	:	:	$Q_0 = 0.70 + 2.34 \sqrt{t}$
No. 10	:	:	:	:	:	$Q_0 = 0.91 + 6.30 \sqrt{t}$

¹⁷ From the records of the Boot Trade Association.

The linearity of the several curves is obviously without question. Here again, we can do little or nothing to determine the asymptotic values since the data are too sparse in the late stages of the experiments.

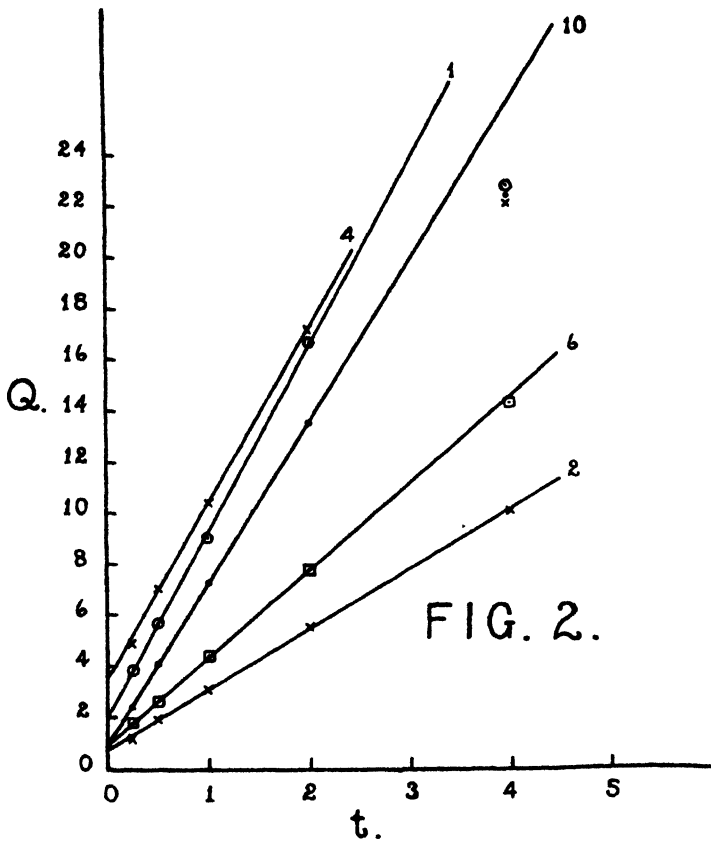


TABLE II.

No. 2.				No. 10.		
t .	Q .	Q_0 .	$Q - Q_0$.	Q .	Q_0 .	$Q - Q_0$.
0.25	1.26	1.29	- 0.03	2.44	2.49	- 0.05
0.50	1.89	1.87	+ 0.02	4.12	4.06	+ 0.06
1.00	3.07	3.04	+ 0.03	7.20	7.21	- 0.01
2.00	5.50	5.38	+ 0.12	13.50	13.50	0.00
4.00	10.00	10.06	- 0.06	22.60	—	—
7.00	16.30	—	—	24.42	—	—
23.00	19.90	—	—	25.90	—	—
47.00	21.00	—	—	26.30	—	—

Now although in cases (I) and (II) above we have only been able to come to a conclusion with respect to the early stages of the absorptions, a comparison between the two brings out a very interesting point. For

if indeed a surface conductivity is operative the nature of the materials suggest that it would be very high for the fibre boards and very small for the waxed upper leathers. Hence we should expect from equations (22) and (23) that the absorption for the fibre boards would indicate a dominant $t^{\frac{1}{2}}$ progression in the early stages while that for the waxed upper leathers would show a dominant t progression, and this is *exactly what the experimental results show*. Hence we see that there is very strong presumptive evidence that the case (A) could adequately represent both cases (I) and (II) which at first sight seemed to require different hypotheses to explain them.

Case (III). Diffusion in Gelatin Gells.¹⁸

We shall now consider some data of Friedmann and Kraemer relating to the diffusion of sucrose in gelatin gells. The experimental procedure was to cover a layer of gel with an equal depth of the solution of sucrose in water. The concentration of the solution was determined at successive intervals of time with a Zeiss Immersion Refractometer. The following Table III is founded on Table II of their paper:—

TABLE III.

t .	Q (obs.).	Q_0 (calc.).	$Q - Q_0$.
8.55	0.0511	0.0508	+ 0.0003
21.08	0.0777	0.0761	+ 0.0016
29.77	0.0908	0.0892	+ 0.0016
45.42	0.1048	0.1086	- 0.0018
53.90	0.1169	0.1178	- 0.0009
70.50	0.1340	0.1337	+ 0.0003
93.90	0.1549	0.1533	+ 0.0016
117.20	0.1700	0.1705	- 0.0005
144.87	0.1904	0.1889	+ 0.0015

Column 3 has been calculated from the equation

$$Q_0 = 0.006496 + 0.01515 \, t^{\frac{1}{2}}.$$

Since the experimental accuracy is estimated as of the order of 1 per cent. the agreement can be regarded as very good. We note that the experiment has not been carried on long enough for there to be any points in the neighbourhood of the asymptote; if there had been, we should have been able to consider the adequacy of a fitting by the equation:

$$Q = 0.006496 + 0.4933 \, \psi(0.001827 \, t)$$

which is got by taking the theoretical asymptote of 0.5 and assuming that the surface conductivity is infinite.

Case (IV). The Swelling of a Laminaria Leaf.¹⁹

This case is to be considered to demonstrate that the diffusion function can often represent data considerably better than the much favoured monomolecular equation.

¹⁸ Friedmann and Kraemer, *loc. cit.*

¹⁹ Freundlich, *loc. cit.*, p. 696.

TABLE IV.

t .	Q (obs.).	Q_0 (calc.).	Q'_0 (calc.).
1	40	27	37
3	96	97	101
5	143	144	153
7	183	183	196
9	216	217	231
11	246	246	260
13	270	272	284
15	294	295	303
18	326	326	326
20	345	343	338
22	360	359	347
24	372	373	355

The observed values of Q in the second column are taken directly from Freundlich's table, while columns 3 and 4 are calculated from the equations

$$Q_0 = -68 + 560 \psi (0.05576 t)$$

$$Q'_0 = 392 (1 - e^{-0.0875 t}).$$

This latter equation is derived by taking the average of the values of $1/t \log (1 - Q/392)$ which Freundlich considers are sufficiently constant to confirm a fitting by the monomolecular equation.

In conclusion, I should like to express my thanks to Mr. H. Bradley for his helpful advice and criticism, also to the Council of the British Boot, Shoe and Allied Trades Research Association, in whose laboratories this work was done, for permission to publish the paper.

REVIEWS OF BOOKS.

Protective Films on Metals. By ERNEST S. HEDGES, M.Sc., Ph.D. (Manchester), D.Sc. (London), A.I.C. Demy 8vo. 276 + xi pages. 23 illustrations. (London: Chapman & Hall. Price 15s. net.)

It is a strange fact that, whilst there exist several books dealing with liquid films, the reader who wishes to study recent work on solid films must usually seek out the original papers, which lie buried in a score of scientific journals. Thus gratitude would be due to anyone collecting the scattered matter within the covers of a single volume. The present volume is, however, particularly to be welcomed, coming from an author who has himself accomplished distinguished experimental work on thin films, and who has shown by his recent book on "Colloids" an unusual power to discuss large and complicated subjects in a simple and interesting manner.

After a brief introduction, Dr. Hedges devotes a long chapter to The Mechanism of Corrosion—a subject so closely interlocked with that of protective films that it clearly cannot be excluded. Apart from an admirable survey of the work and views of various investigators, the Author presents a valuable—and in some respects novel—view of the mechanism of the hydrogen-evolution type of corrosion. He suggests that the metal first reacts with water eliminating hydrogen and producing a coat of metallic hydroxide, which will put a stop to further attack, unless it is removed by dissolution or peptisation by acid, salt or alkali present; it is the rate of this removal which determines the effective rate of corrosion. This theory at once suggests why aluminium is dissolved more quickly by hydrochloric than by sulphuric acid, and more quickly still by sodium

hydroxide; it would seem also to explain the fact that the dissolution in hydrochloric acid is proportional to the third power of the concentration of *undissociated* molecules of hydrogen chloride. The suggestion that water plays a primary rôle in the production of hydrogen is put forward cautiously; Dr. Hedges himself describes the view as heterodox, but heterodox theories are worth careful consideration if they explain facts about which the orthodox are silent. The new theory, however, may require a little development, if it is to explain Palmaer's recent work on the effect of purity upon the rate of attack.

The subject of protective oxide-films is next discussed, with a good description of the formation, isolation and thickness of the films present on different metals. The following chapter, entitled "Protective Films Formed during Atmospheric Corrosion," is devoted mainly to the important work of Vernon, whilst the chapter on "Protective Films in Liquid Media" contains a welcome account of Dr. Hedges' own researches on the behaviour of iron in nitric acid, which have disposed finally of the argument often advanced by armchair critics that the passivity of iron in nitric cannot be due to an oxide film, since the acid would dissolve it; not only did Dr. Hedges show that nitric acid has practically no solvent action for anhydrous ferric oxide when cold, but that the temperature at which dissolution becomes appreciable is the very temperature at which the passivity of the metal breaks down. A long chapter on anodic films deals partly with the well-known work of W. J. Muller at Vienna, and partly with the very detailed study of periodic film formation carried out in London, on twelve different metals, by Dr. Hedges himself.

The last six chapters deal with the practical applications of protective films. The artificial production of skins on ordinary steel, the natural skins present on "stainless" steels, the production of metallic coats and alloy coats, by hot dipping, electro-plating, spraying or cementation, receive attention in turn; in every case, the practical problems involved are discussed from a strictly scientific standpoint. The subject of protection by paints, varnishes and enamels receives brief treatment in an appendix.

The whole book is written in a clear and interesting manner, and it is difficult to overestimate the service that Dr. Hedges has performed in extracting the important features of long and sometimes "unreadable" papers, and setting them forth in a form capable of being appreciated by readers whose time is limited. Moreover—unlike so many scientific books, which are out-of-date on the day of publication—the volume contains references to many of the most recent developments of the subject. Of criticism there is little need. It is likely that some electrochemists would challenge certain statements made in the second chapter during the discussion of electrode potentials, couples and short-circuited cells; but it is doubtful whether any author has succeeded in producing an elementary treatment of these matters without giving offence. The statement in the introduction that "a discontinuous film is generally worse than the total absence of a film" appears too strong. It is true, as the Author states, that the exposed parts of faultily copper-covered iron corrode—under certain conditions—more intensely than if the whole iron surface were bare; but this is not always true even with copper coats, whilst with coatings of most other metals, the intensification of attack is very rarely met with; an imperfect plating of nickel, for instance, is—under ordinary conditions—distinctly better than no plating at all. This, however, is merely mentioned as a very small point for consideration during the preparation of the second edition, which will certainly be called for in due course. For the rest, the publishers have done their part well, by excellent printing, whilst the diagrams are all that can be desired. The book—which demands very little knowledge of physics, chemistry or mathematics—should make an appeal to the technical metallurgist and engineer as well as to the pure scientist.

U. R. E.

THE ELECTRO-DEPOSITION OF IRON-COBALT ALLOYS. PART I.

BY S. GLASSTONE AND J. C. SPEAKMAN.

Received 21st July, 1932.

The cathodic deposition of alloys of the iron-group metals forms a specially interesting study, because in the first place these metals are completely soluble in each other in the solid state, and in the second place they show a high overvoltage for deposition. Glasstone and Symes^{1, 2} have given an account of the electro-deposition of iron-nickel alloys, and Glasstone and Speakman^{3, 4} of the deposition of cobalt-nickel alloys; the present paper deals with a similar study of the iron-cobalt series. Previous work in this connection has been even more scanty than on the other alloys, the results being so few as to have little value, for reasons given previously.⁵ Toeppfer⁶ found that at C.D.'s between 0.21 and 4.2 amps. per sq. dm. a solution of ferrous and cobalt sulphates, in which 10 atomic per cent. of the total iron and cobalt was iron,⁷ gave alloys containing 13 per cent. of iron, whereas Bruni and Amadori⁸ stated that for low C.D.'s the composition of the deposit was independent of that of the solution, provided the latter contained between 33 and 50 per cent. of iron.

The work to be described was carried out under a wide range of conditions. The deposits were made from buffered solutions of carefully regulated p_H values, containing ferrous and cobalt sulphates, and the results reported here show the effects on the composition of the deposited alloy of: (i) C.D., (ii) the proportion of iron and cobalt in the electrolyte, (iii) its total concentration, (iv) its p_H value and (v) stirring.

Experimental.

The experimental details were similar to those of Glasstone and Symes¹ and Glasstone and Speakman.³ The ferrous sulphate was of A.R. quality; the cobalt sulphate contained about 1 per cent. of iron, but allowance was made for this in making up the electrolytes. The acetate buffers of p_H 's 3.2, 4.0 and 5.2 used as a basis for these solutions were of the same compositions as had been used previously (*loc. cit.*). As in the work on iron-nickel alloys the catholyte was placed in a porous pot in order to avoid the oxidation of the ferrous ions at the anode; the anolyte which surrounded the porous pot consisted of buffer solution

¹ *Trans. Faraday Soc.*, **23**, 213, 1927.

² *Ibid.*, **26**, 565, 1930.

³ *Ref. (1)*, p. 214.

⁴ *Ibid.*, **24**, 370, 1928.

⁵ *Ibid.*, **27**, 29, 1931.

⁶ *Z. Elektrochem.*, **6**, 347, 1899.

⁷ Throughout this paper the convention will be adopted of referring to such a solution as one containing "10 per cent. of iron," or "10 per cent. Fe."

⁸ *Atti. Accad. Sci. Padova*, **30**, 349, 1910.

734 ELECTRO-DEPOSITION OF IRON-COBALT ALLOYS

only. The following electrolytes were used in the course of the present work, the total concentration "(Fe + Co)" being expressed in g. equivs. per litre:—

Solution.	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.	XI.
p_H	3.2	3.2	4.0	4.0	4.0	4.0	4.0	5.2	4.0	4.0	4.0
(Fe + Co).	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	0.4	0.4	0.4
Fe per cent.	10	50	3	10	30	50	70	50	10	30	50

All depositions were made at room temperature (about 16°).

Adjustment of Hydrogen-Ion Concentrations.—The evolution of hydrogen at the cathode during alloy deposition caused the catholyte to become more alkaline during electrolysis, and this was counteracted by the periodic addition of *N*-acetic acid solution containing the dissolved salts in the appropriate concentrations. The rate of addition of acid was found to be given by the formula:

$$\text{Rate} = Ki(1 - e),$$

where i is the current, e the current efficiency and K a constant which depends only on the composition of the buffer solution; the value of the constant was also the same when it was calculated for the results which had been obtained in the work on iron-nickel and cobalt-nickel alloys. The p_H value of an acetate buffer solution depends on the ratio: [undissociated acetic acid]/[acetate ion], and when hydrogen ions are discharged at the cathode, ionisation of the undissociated acetic acid takes place, so that the above ratio decreases pending adjustment; on the basis of these facts a value of K may be simply calculated theoretically. The values calculated agree with those found empirically as closely as could be expected.

The p_H values of the solutions were checked from time to time by means of indicators (generally brom-phenol blue). A slight difficulty was encountered in this connection when it was found that electrolytes which had been in use for a few days gave unexpectedly low values of p_H ; this error was traced to the adsorption of indicator by colloidal material which was produced by atmospheric oxidation and hydrolysis of the ferrous sulphate.

Analytical Method.—The alloys were dissolved from the copper cathodes, on which they had been deposited, by a mixture of dilute sulphuric acid and hydrogen peroxide. After the solution had been boiled to destroy excess peroxide, copper was removed by passing hydrogen sulphide, which also reduced the iron to the ferrous state. The filtered solution, freed from hydrogen sulphide by boiling, was titrated with approximately 0.03 *N*-permanganate solution; this titre corresponded to the amount of iron in the deposit. The method of estimating the cobalt was based on one recommended by Willard and Hall⁹; the solution from the permanganate titration was made alkaline with caustic soda, treated with sodium perborate, which oxidises iron and cobalt to the tervalent condition, and boiled for ten minutes to decompose excess of perborate. After cooling the cobaltic compound was reduced by adding a known volume of approximately 0.03 *N*-ferrous sulphate dissolved in 10 *N*-sulphuric acid; when the liquid became clear it was

⁹ *J. Amer. Chem. Soc.*, 44, 2237, 1922.

back-titrated with the same permanganate as had been used previously. The difference between this titre and one obtained in a "blank" experiment with no cobalt present gave the amount of cobalt in the alloy. A correction had also to be made to allow for the effect of manganous ions resulting from the first permanganate titration, for they are oxidised by the perborate and reduced by the ferrous sulphate, just as are the cobalt ions. The amount of the correction needed was proportional to the first permanganate titre, as was expected, but it did not seem to correspond to oxidation of the manganese in any simple stoichiometric proportion. The result arrived at empirically was that 1.00 c.c. of permanganate in the first titration accounted for 0.29 c.c. in the second, under the conditions of the present work.

By this method a complete analysis could be made rapidly by means of two titrations in a single solution, a matter of great convenience when a large number of deposits had to be analysed. A further advantage was that since ratios only are involved it was not necessary to know the exact concentration of the permanganate solution. The accuracy of the results was not high, but was sufficient for the purpose, since unavoidable variations in the conditions of deposition account for a considerable uncertainty.¹⁰

Results.

From each solution depositions were made at a series of C.D.'s within the range 0.02/12 amps. per sq. dm. The results have been plotted and smooth curves drawn through the points (Figs. 1, 2 and 3); these curves

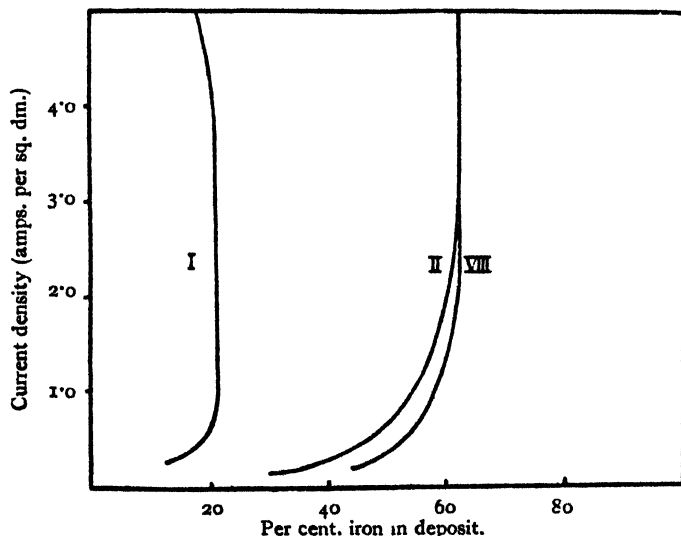


FIG. 1.

show the variation of the amount of iron in the deposits with C.D., for each electrolyte.

Current Efficiency.—The current efficiencies for metal deposition were irregular and much less reproducible than those for the deposition of cobalt-nickel alloys; approximate values are given in Table I.

¹⁰ Ref. (1), p. 217.

The general tendency is for an increase of C.D. and p_H value to increase the current efficiency.

TABLE I.

C.D.	Per cent. Current Efficiency.		
	p_H 3'2.	p_H 4'0.	p_H 5'2.
0.5	15	20-30	50
1.0	30	40-50	c. 100
5.0	35	60-80	c. 100

Physical Characteristics of Deposits.—In general the quality of the deposits was not good, but this was no doubt partly due to the fact that the conditions were not chosen with a view to good quality deposits. Alloys richer in cobalt were generally

brighter and smoother than those rich in iron; stirring tended to improve the quality, but at very low or very high C.D.'s poor deposits were obtained.

"Maxima" and "Minima".—It will be seen from Fig. 1, which contains the curves for solutions of p_H 4.0 and total concentration of (Fe + Co) two g. equivs. per litre, that for any particular solution the

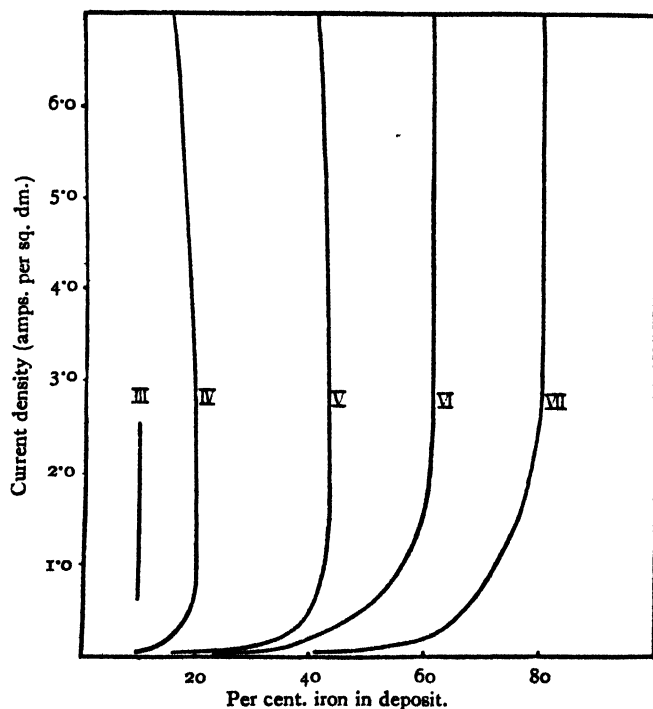


FIG. 2.

alloys deposited at very low C.D.'s contain relatively more cobalt than do the electrolytes. Since the composition of the deposit is changing very rapidly with C.D. in this region, it is difficult to estimate the composition of the "initial deposits." The curves shown, however, are only taken as far as the lowest C.D. at which a deposit capable of analysis was obtained. They indicate an upper limit for the minimum percentage of iron in the deposits; the actual figures are given in Table II.

TABLE II.—COMPOSITIONS OF "INITIAL DEPOSITS."

Fe per cent. in Solution . . .	10	30	50	70
Minimum Fe per cent. in Deposit.	< 9	< 15	< 23	< 40

As the C.D. is increased the proportion of iron in the deposit increases rapidly at first, then more slowly, until a constant "maximum" is

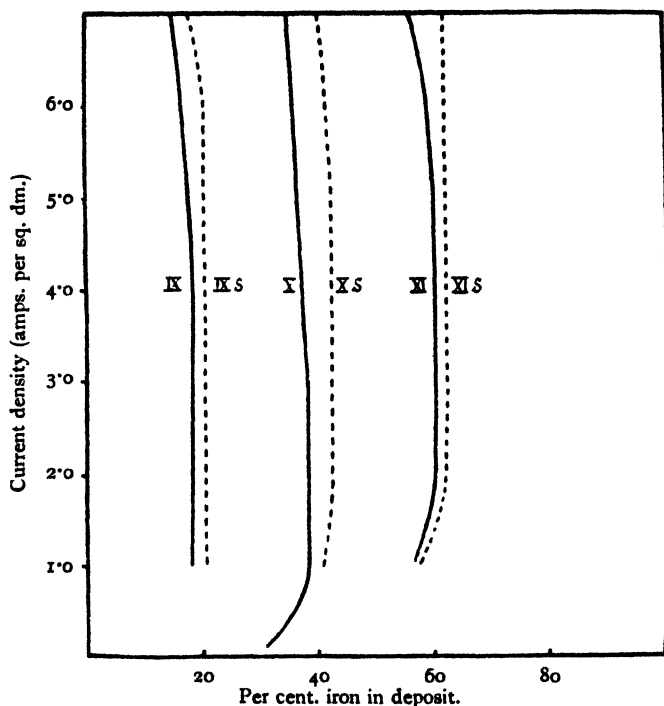


FIG. 3.

attained, which is independent of C.D. up to high values. The maximum percentage of iron in the deposit is always somewhat higher than that in the solution; this is clearly shown in the results in Table III.

TABLE III.—MAXIMUM FE PER CENT. IN DEPOSITS.

Fe per cent. in Solution . . .	3	10	30	50	70
p_H 3.2	—	21	—	62	—
p_H 4.0	10	20	43	61	80
p_H 5.2	—	—	—	62	—

These figures show further that, in agreement with previous work,^{1, 2, 3, 4} the composition of the "maximum" deposit is independent of the p_H of the solution.

Influence of Dilution and Stirring.—With the more dilute electrolytes (Solutions IX, X, XI; see Fig. 3) the maximum percentages of iron in the deposits were slightly lower than those quoted in Table III; they were 18, 38 and 61 per cent. respectively, as compared with 20, 43 and 62 per cent. of iron. In these cases too there is a tendency for the iron content of the deposit to decrease again at very high C.D.'s; both these effects could be counteracted by stirring as the curves marked "S", and dotted, in Fig. 3 indicate.

Discussion.

The results given here may be readily correlated with the views developed previously.¹¹ The cathodic deposition potentials of iron-cobalt alloys increase rapidly at first as the proportion of iron in the electrolyte is increased (— 0.56 volt for pure cobalt to — 0.64 for 50 per cent. Fe, in solution) and then more slowly (— 0.68 volt for 100 per cent. Fe).¹² These facts suggest that the presence of a comparatively small proportion of iron has a relatively large effect in raising the overvoltage for cobalt deposition; this effect is similar to, but less than, that of iron on the deposition of nickel. In terms of the theory that the overvoltages of these metals are due to primary deposition in a metastable form¹³ it may be stated that iron retards the rate of transformation of cobalt from the metastable to the stable form.

From any solution of ferrous and cobalt sulphates the "initial deposit" will consist largely of cobalt since it has the less negative deposition potential. The deposit will, however, contain a small proportion of iron because of the miscibility of the metals in the solid state; the iron retards the transformation of cobalt, so that the deposition potential becomes more negative. The deposition of a larger proportion of iron will thus be favoured, and this will have a correspondingly greater retarding effect. The proportion of iron in the deposit will therefore increase rapidly as the C.D. is raised from very low values. Ultimately two factors will tend to prevent further increase: (a) local relative depletion of ferrous ions in the solution near the cathode, because of the high proportion of iron in the deposit, and (b) depolarisation of the cathode for cobalt deposition because it contains a high proportion of the other metal in solid solution. Under the influence of these factors the proportion of iron in the deposit will reach a maximum value, which remains constant until at very high rates of deposition depletion of the electrolyte near the cathode will cause a falling off. The C.D. at which the maximum is reached is lower the greater the p_H of the electrolyte; this is due to the fact that the rate of metal deposition increases (see Table I) with increasing p_H . For the same reason the C.D. at which the proportion of iron begins to fall off from the maximum value with increasing C.D. is lower the lower the hydrogen-ion concentration of the electrolyte. As already noted (Table III) the actual proportion of iron in the alloy when the maximum is attained is independent of the p_H of the solution.

If the total concentration of the solution is decreased the exhaustion of ions from the neighbourhood of the cathode will occur more easily; the maximum proportion of iron in the deposits should thus be somewhat less than from a more concentrated solution containing iron and cobalt in the same ratio. The C.D. at which the falling off in iron content is

¹¹ Ref. (1), p. 220.

¹³ Glasstone, *J. Chem. Soc.*, 2899, 1926.

first noticeable should also be lower in a more dilute solution. These forecasts are in agreement with actual observation, as may be seen by comparing curves IV and IX, V and X, and VI and XI (Figs. 1 and 3). The effect of stirring a dilute solution is of course to counteract the tendency for the local depletion in concentration of the electrolyte, so that the results are more like those with a more concentrated solution (*cf.* curves V and X S, VI and XI S).

Comparison of the Behaviour of Iron-Cobalt, Iron-Nickel and Cobalt-Nickel Alloys at 15°.—The three pairs of alloys fall into a natural order, *viz.*, iron-cobalt, iron-nickel and cobalt-nickel; in each pair the former metal (referred to as A) fulfils analogous functions with reference to the second (B). An interesting gradation is shown when comparing, as in Table IV, the maximum proportions of A deposited at room temperatures from corresponding solutions of total concentration 2.0 N; the deposition potential of each metal is placed below its name in the table.¹²

In the first series of alloys the deposits at low C.D.'s from all solutions were found to contain a defect of A (iron) as compared with the proportion in the electrolyte; the "initial deposits" may well consist of almost pure B (cobalt). In the second series this effect is modified;

TABLE IV.

A per cent. in Solution.	Maximum A per cent. in Deposit.		
	Iron-Cobalt. — 0.68 — 0.56.	Iron-Nickel. — 0.68 — 0.57.	Cobalt-Nickel. — 0.56 — 0.57.
10	20	46	57
30	43	77	82
50	61	87	92

from some solutions deposits were obtained with a defect of A (iron), but from others this was not the case. In the third series no lower proportion of A (cobalt) than the maximum, which was greater than that in the solution, could ever be realised even at the lowest C.D.'s attainable.

The assumption that in each series the metal A exerts a retarding effect on the deposition of B, taken in conjunction with a knowledge of the deposition potentials quoted in Table IV, enables the gradation to be accounted for. In the first two series there will obviously be a tendency initially for a larger proportion of B to be deposited since in each case the deposition potential is less negative than that of A (iron). The retarding effect of A is, however, greater in the second than in the first case, as may be seen from a comparison of the deposition potentials of iron-cobalt and iron-nickel alloys from solutions of similar compositions.¹² It is to be expected therefore that the proportion of A (iron) in the deposit will increase more rapidly with increasing C.D. and will reach a higher maximum value in the second case than in the first; this has been found experimentally to be the case (see Table IV and Ref. 1). In the cobalt-nickel series the deposition potentials of alloys of all compositions are so nearly identical that the existence of a retarding effect cannot be deduced in the same way as for the other pairs of metals; that such an effect is operative is shown, however, by the fact that the maximum proportion of A in the deposit is so high.³ In this case, where there is no appreciable initial tendency towards the deposition

of B, the deposition potentials of A and B being so close together, the retarding influence of A on B is very effective. For the same reason there will be no tendency for the composition of the alloy to change with C.D., so that the maximum proportion of A will be attained at very low C.D.'s if not in the actual "initial deposit."³

Summary.

1. A study has been made of the compositions of the alloys deposited from well buffered solutions, of definite hydrogen-ion concentrations, containing various proportions of ferrous and cobalt sulphates over a range of C.D.'s.

2. From each solution the amount of iron in the deposit was found to increase with increasing C.D. until a maximum was attained; beyond this point further increase of C.D. has no effect on the composition of the deposit until very high C.D.'s were reached, when the proportion of iron decreased slightly.

3. The composition of the alloy of maximum iron content obtained from a solution containing a given proportion of iron to cobalt is independent of the p_H value of the solution; this deposit always contains relatively a larger proportion of iron than the solution. The actual composition of this alloy is somewhat affected by the total concentration of the solution and by stirring.

4. The deposits obtained at very low C.D.'s contain relatively less iron than do the solutions.

5. The results are discussed from the standpoint of the deposition potentials of iron, cobalt and their alloys.

6. A general review is presented of the results obtained in studies of the deposition of iron-cobalt, iron-nickel and cobalt-nickel alloys at ordinary temperatures.

*The University,
Sheffield.*

THE PASSIVITY OF GOLD.

BY WILLIAM JAMES SHUTT AND ARTHUR WALTON.

Received 25th July, 1932.

It has been shown by Stirrup and one of us¹ that a gold or iron electrode, anodically passivated in certain electrolytes, requires a definite time interval after stoppage of the passivating current for complete recovery of the active state. This time of recovery is readily reproducible under given conditions and decreases with rise of temperature in a manner which gives every indication that the recovery process is a chemical reaction. W. J. Müller² suggests that the measured time may be taken as the time required for solution of an anodic film in the electrolyte. Although this view no doubt broadly expresses the facts, it cannot be assumed that the recovery process is a simple reaction.

Bound up, as it must be, with the high back E.M.F. of a passive electrode, the elucidation of nature of the film on an already passivated

¹ W. J. Shutt and V. J. Stirrup, *Trans. Far. Soc.*, **26**, 635, 1930.

² W. J. Müller, *Trans. Far. Soc.*, **28**, 471, 1932.

metal seems a matter of urgent importance, and the following work on the mechanism of the recovery process was undertaken with a view to contributing further towards the solution of this problem.

Experimental.

The object of the research being a study of the reactivation of a passivated gold anode, by observation of the potential changes after interruption of the passivating current, it became of first importance that the measuring instruments should cause no depolarisation of the electrode, but should allow the latter to behave as though electrically isolated in solution. With this point in view the experimental arrangement in Fig. 1 was constructed.

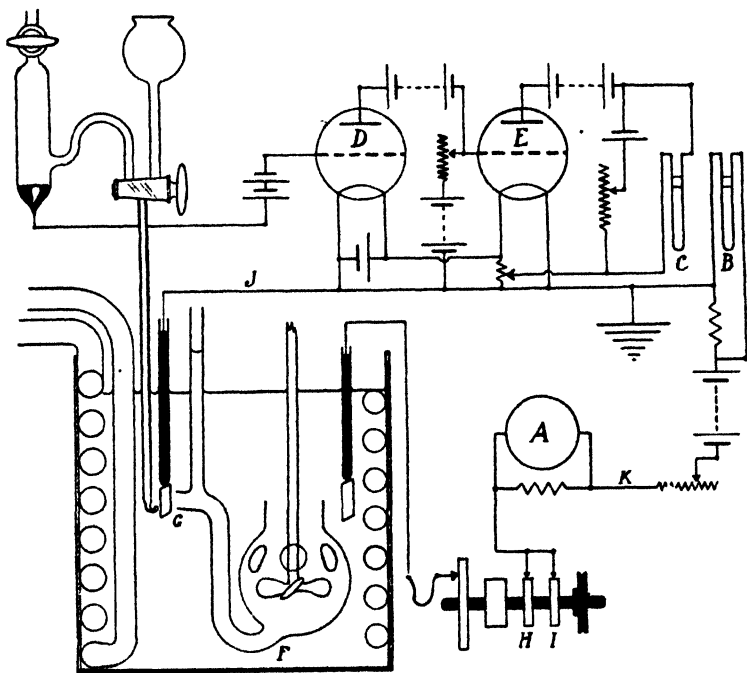


FIG. 1.

The commutator and current measuring instruments—the ammeter A and shunted oscillograph vibrator B—used by Shutt and Stirrup, were retained, but the second vibrator C was coupled with a two-valve amplifier to act as a recording voltmeter of extremely high resistance. The potential of the gold anode against a normal calomel electrode, the tip of which was placed at the side of the metal electrode, was impressed on the grid of a thermionic valve D which was battery-resistance coupled to a second valve E, the output of which was of a suitable magnitude for observation on the high frequency Dudell oscillograph employed. This voltmeter system was calibrated against Weston cells after each series of measurements. The electrolyte was contained in a glass vessel 6 inches diameter by 6 inches deep, fitted with a glass coil through which water from a thermostat could be circulated, the temperature of the electrolysis cell being by this means maintained within 0.02°C .

In view of the heterogeneous nature of the processes under consideration, it became necessary to investigate further the effect of stirring the electrolyte. To do this two methods of stirring were adopted, these are referred to later in the text as S and D respectively. In the series of experiments labelled S, the electrolyte was stirred as vigorously as possible. This was effected by the device shown diagrammatically in Fig. 1. It consisted of a perforated glass bulb, open at the top, with an outlet tube F sealed on at the bottom, and bent round to face the electrode at G. The electrolyte was forced, by means of the rapidly rotated glass propellor, through F directly over the surface of the electrode. Experiment showed that this method of stirring was much more efficient than any other system of mixing. In the second series of experiments, no attempt was made to force the electrolyte over the electrode, but the stirrer was used to produce a general mixing of the electrolyte, in order to minimise any effects due to local changes in concentration caused by the electrolysis.

The anodes were plates of assay gold 10 mm. by 5 mm. in area, coated on the back and sides with fusible enamel glass, in such a way that only the face was in contact with the solution, and so enabling the current density to be defined.

A time record was printed on each oscillogram with the aid of a relay, operated by mercury contacts on the pendulum of a clock. The relay controlled a shutter, interposed between the fixed mirror of the oscillograph and the sensitive paper in the recording camera.

Results.

The potential changes which occur during the spontaneous recovery of the active state at a passivated gold anode are shown in Fig. 2, which

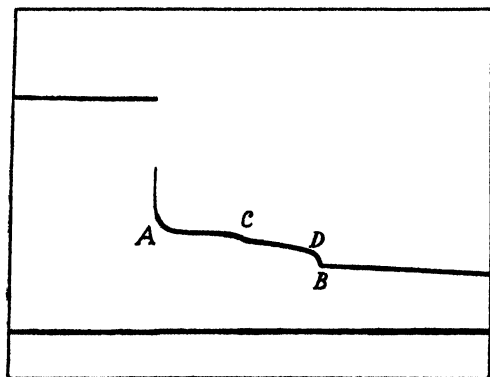


FIG. 2.

is a reproduction of a typical oscillogram, the ordinates representing potentials against *N* calomel, and the abscissæ time. Immediately following the interruption of the passivating current at A, there is an abrupt fall in the potential, which then remains almost constant until the point C is reached. At C there is a point of inflection. This is followed by a further slow fall in voltage until D is reached, after which the

process is completed by a final rather sudden drop to B, where the break in the curve, as the electrode assumes the normal potential of active gold, is extremely well marked. The time AB which is referred to in this paper as the "total time of recovery of the electrode," has been measured under a wide variety of conditions.

In the work of Shutt and Stirrup the time of recovery was determined by measuring the maximum period of rest which could be imposed by the commutator without allowing the passivated gold to become active.

The persistence of the passive form was indicated by the immediate evolution of chlorine, at its characteristically high anodic potential, on closing the circuit again. The point of recovery in this sense was quite definite and was readily shown by means of the improved measuring apparatus of Fig. 1 to coincide with the point D of Fig. 2. Thus the time of recovery measured by Shutt and Stirrup corresponds to the length AD and is slightly shorter than the total time of recovery as considered here.

It was of interest to determine whether there could be any partial recovery of activity, which might possibly be shown by applying a small current at points on the curve either between A and C or C and D. The experimental arrangement in Fig. 1 was therefore modified as follows. The slip rings H and I of the commutator were connected by resistances of widely differing numerical values to the negative pole of a 24 volt battery. By this means the electrode could be passivated during connection with one segment of the commutator, while the other segment would complete the circuit through such a high resistance that only a few milliamperes would pass through the cell. With the smaller current having a value of only 10 m.a. per sq. cm. the results indicated that the recovery process was divided into two parts. If the time of rest allowed by the commutator after passivation were less than that represented by AC of Fig. 2, the electrode immediately assumed the potential necessary for chlorine evolution, and the passive state persisted indefinitely, even at this low current density; if, however, the 10 milliamperes circuit were completed during the period CB, the anodic potential rose a little at first, but then continued to fall to the break B, where the gold dissolved actively, *i.e.* the recovery process was completed just as in the absence of current, the only change being a slight lengthening of the time involved.

When the second current was increased above 10 m.a. to the order of, but still below, the limiting current required to cause passivation of an active electrode, the time which had to elapse to prevent passivation was always greater than AC but less than AD. Under these conditions also, if immediate repassivation did not occur, on closing the lower current circuit, the electrode became completely active as before.

An attempt to determine the time of recovery in solutions of different concentrations of hydrochloric acid showed that a number of conditions must be taken into consideration before a definite value for a time of recovery could be given for any one strength of acid. In the work of Shutt and Stirrup no attention was given to the effect of current density after the electrode was passive; the passivating current density only was considered. A series of measurements have been made where the effect of the increase in potential on passivation upon the value of the current density was masked by using a higher voltage in series with a large resistance, so that the passive current density was practically the same as the initial current density. In these experiments, to prevent arcing at the contact, the commutator was used to operate a relay which broke the actual current in the circuit. Table I shows the variation of the time of recovery in 1.0 normal hydrochloric acid at 25° C. for the two types of stirring described above, and with varying current densities.

It will be seen that the time of recovery in the more vigorously stirred electrolyte varies considerably with the current density, whilst, although the time is longer in the less stirred solution, the variation with current density is much less marked.

The variation of the time of recovery with temperature at a constant

TABLE I.—THE TIME OF RECOVERY OF GOLD IN 1.0 N HCl AT 25° C.

Stirring: S.		Stirring: D.	
C.D. (Amps./cm. ²).	Time (Seconds).	C.D. (Amps./cm. ²).	Time (Seconds).
0.90	0.670	0.32	0.98
0.91	0.665	0.42	1.02
1.02	0.660	0.56	1.08
1.21	0.667	0.83	1.04
1.36	0.725	1.00	0.94
1.48	0.769	1.25	1.01
		1.42	1.01

current density of 1.50 amps./cm.² is shown in Table II, and it is at once evident that the temperature coefficient is of the order of that required by a chemical reaction, and that the constancy for the value of Q in the Arrhenius equation $\log \frac{K_2}{K_1} = \frac{Q}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$ is all that could be expected. Values of Q are given in column 4 of the table. For this calculation $\frac{K_2}{K_1}$ is assumed to be identical with $\frac{\theta_1}{\theta_2}$, where θ_1 and θ_2 are times of recovery at the temperatures T_1 and T_2 respectively.

TABLE II.—EFFECT OF TEMP. ON THE TIME OF RECOVERY OF GOLD IN N HCl.

C.D. 1.50 amps./cm.² STIRRING: S.

Temp.	Time of Recovery. (Seconds.)	Temp. Coeff.	Q , (Cals.)
14.9	2.10	—	—
24.9	0.77	2.73	17230
34.9	0.35	2.20	14460
45.0	0.174	2.01	13540
55.4	0.0845	2.06	14510
65.4	0.044	1.92	14500

In the previous experiments little account was made of the presence of chlorine in the solution, although there must always have been some present as a result of the preliminary polishing given to the anode with that gas. Further experiments, particularly with weak solutions and at low temperatures, showed that the effect of chlorine was considerable; it was also apparent that the time for which the electrode was evolving chlorine was of equal importance. Whilst the difficulties of using an enclosed electrode prevented a full investigation into the effect of chlorine, some figures, which are shown

TABLE III.—THE EFFECT OF CHLORINE ON THE TIME OF RECOVERY.

Time of Passage of Chlorine. (Minutes.)	Time of Recovery. (Seconds.)
0	8.5
10	9.5
20	13.5
30	16.5

in Table III, were obtained for the time of recovery in 0.125 N HCl before and after bubbling chlorine gas into the solution.

If the passivating current were maintained for some time, a further increase in the time of recovery was noted, thus after 1 minute the time of recovery in the above solution rose to a value of 35 seconds; prolonging of the electrolysis beyond this time, however, led to no further increase in the time of recovery. It was also noted that the presence of chlorine in the solution led to an increase in the potential of an active gold electrode of about 0.18 volt. It should be noted that the effect of chlorine on the time of recovery became much less marked as the concentration of electrolyte was increased above 0.125 normal.

The relation between time of recovery and concentration of hydrochloric acid is shown in Table IV. These figures were obtained in solutions containing a considerable, and as far as possible constant, quantity of chlorine.

TABLE IV.—CHANGE OF TIME OF RECOVERY WITH CONC. OF HCl.

Temperature, 25° C. Stirring : S.

Conc. of HCl. (Normality.)	C.D. (Amps./cm. ²)	Time of Recovery. (Seconds.)
4.0	2.5	0.032
2.0	1.5	0.18
1.0	1.5	0.77
0.75	1.3	1.38
0.50	0.7	2.9
0.25	0.3	12.8

With a view to differentiating between the effects of hydrogen ion and chloride ion on the rate of recovery of activity, a series of experiments were carried out with mixtures of KCl and HCl. The results for measurements made in presence of a total concentration of chloride of one mole per litre and with varying hydrogen-ion concentration are given in Table V

TABLE V.—TIME OF RECOVERY OF GOLD IN SOLUTIONS 1.0 NORMAL IN CHLORIDE ION.

Conc. of H ⁺ (Normality).	Time of Recovery (Secs.)		Conc. of H ⁺ (Normality).	Time of Recovery (Secs.)	
	S.	D.		S.	D.
Temp. 25° C. ; C.D. 0.76 amps./cm. ²			Temp. 35° C. ; C.D. 0.76 amps./cm. ²		
0.500	0.70	0.94	1.00	0.31	—
0.377	0.79	1.03	0.500	0.38	0.47
0.263	0.98	1.30	0.401	0.42	0.51
0.158	1.32	1.60	0.308	0.45	0.57
0.115	1.57	1.94	0.263	—	0.62
0.084	1.86	2.29	0.221	0.58	0.70
0.051	1.94	2.90	0.179	0.62	0.79
0.017	4.52	4.72	0.138	0.71	0.86

for the two temperatures 25° C. and 35° C. These and similar results for 0.75 N and 2.0 N chloride at 25° C. are expressed graphically in Fig. 3, where total times of recovery in seconds are represented vertically and the reciprocals of the hydrogen-ion concentration appear as abscissæ. This diagram also indicates the change in the time of recovery with

alteration in the rate of stirring; the full lines represent results obtained in well stirred solutions (S) and the broken lines refer to conditions of only diffuse mixing of the electrolyte (D). In addition Fig. 3 illustrates the effect of current density at the passive electrode before reactivation commences. Except in the case of curves A and B where the current densities were 0.87 and 1.3 amps./cm.² respectively, all measurements were made on electrodes at which the current density immediately before switching off the current had been 0.76 amps./cm.² In order that conditions should be as far as possible comparable, each recovery was measured after the passive electrode had been evolving chlorine for some seconds.

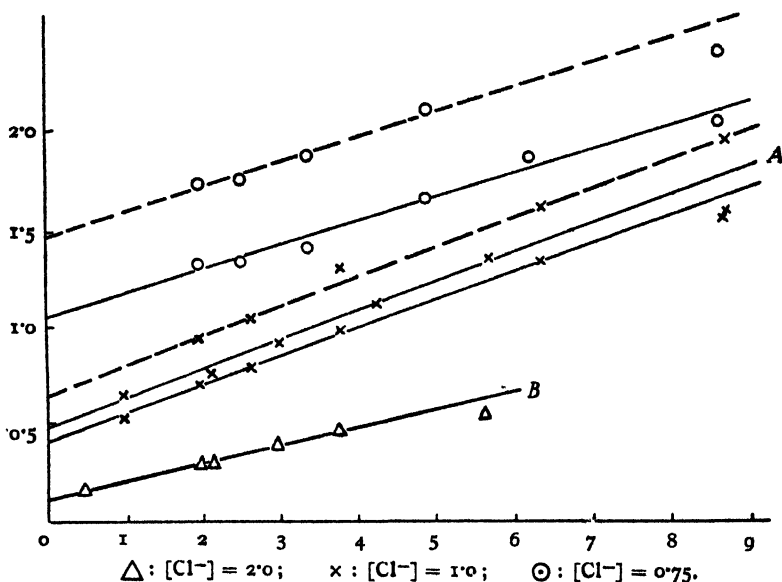


FIG. 3.

The total time of recovery θ may be represented by an equation of the form,

$$\theta = \frac{K}{[H^+]} + \theta_{Cl},$$

where both K and θ_{Cl} are constants for any one concentration of chloride. With increasing chloride ion in solution, however, while K changes little, values of θ_{Cl} decrease rapidly. For 0.75, 1.00 and 2.00 N chloride, in well stirred solution, values of θ_{Cl} are 1.06, 0.41 and 0.12, respectively, *i.e.* θ_{Cl} decreases more rapidly than the square of the concentration increases but not so rapidly as the cube. For the concentrations of 1.00 N and 0.75 N chloride, in electrolyte diffusely mixed, the corresponding values of θ_{Cl} are 0.65 and 1.47. The effect of stirring is interesting. The value of K is apparently entirely unaffected by an increased rate of flow of the electrolyte over the electrode; θ_{Cl} , however, is considerably decreased. An increase in passivating current density brings about results exactly analogous to those caused by a decrease in stirring, *i.e.* K remains constant but θ_{Cl} increases. The effect of temperature on the quantities K and θ_{Cl} was determined by making a

series of measurements with 1.0 *N* total conc. of chloride at 35° C. The results compared with analogous figures for 25° C. are given in Table VI.

TABLE VI.—EFFECT OF CHANGE OF TEMP. ON THE VALUES OF *K* AND θ_{Cl} .

Temp.	<i>K</i>		θ_{Cl}	
	S.	D.	S.	D.
25° C.	0.145	0.145	0.41	0.61
35° C.	0.078	0.090	0.22	0.29

It is important to note that the value of these results may be to some extent vitiated by an unknown effect of temperature on the effectiveness of the stirring employed, and on the concentration of chlorine in the solution.

For low concentrations of hydrogen ion, the relation $\theta = \frac{K}{[H^+]} + \theta_{Cl}$ no longer holds, the experimental values of θ falling considerably below those predicted by the equation. The behaviour of the electrode in a neutral solution of KCl indicates a possible reason for these discrepancies at low acidity. If the electrolyte be vigorously stirred, the electrode does not recover at all in such a solution. When, however, in absence of stirring, the products of electrolysis are allowed to accumulate round the electrode, then recovery occurs in about four or five seconds. It is suggested that recovery is in this case brought about by the products of electrolysis—mainly HOCl and HCl produced by the hydrolysis of chlorine. Thus the discrepancies observed in solutions only weakly acid might be due rather to a faulty estimate of the nature of the electrolyte than to any failure of the straight line relation postulated above.

The preceding results show the time of recovery of a passive electrode, allowed to recover spontaneously. Some measurements have been made of the quantity of electricity necessary to

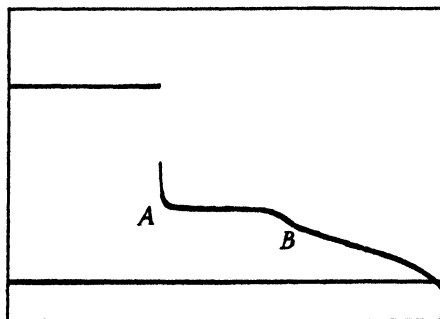


FIG. 4.

cause recovery of the electrode by cathodic reduction. In order that a true estimate might be made of the time necessary to cause recovery solely by cathodic means, the experiments were conducted in solutions of hydrochloric acid so dilute that the rate of spontaneous recovery was negligibly small. A modification of the circuit in Fig. 1 was used. A battery of 40 volts was connected through a series resistance of several thousand ohms to the points J and K in the diagram to oppose the main passivating current. A small switch, not shown in the figure, was used to safeguard the ammeter. The effect of this arrangement was that as soon as the main circuit was opened, a current of a few milliamperes flowed in the opposite direction. The shape of the voltage curve with time is shown in Fig. 4. From A to B the cathodic current is reducing the film

on the electrode. At B the electrode is active, since this point is below the value of the potential observed for an active gold electrode standing in the solution. As might be expected, the results obtained for the time AB varied with the conditions before switching off. The time of reduction increased with the passivating current employed, with the length for which the anode had been held passive, and also with decrease in the efficiency of stirring. These effects are probably all due to the greater quantity of chlorine in the vicinity of the electrode requiring reduction. The use of a smaller current for reduction resulted in a proportionately longer time. Table VII shows the quantity of electricity required to cause reduction in solutions of 0.125 *N* and 0.25 *N* HCl for several values of the passivating current, and of the reducing current.

TABLE VII.—THE NUMBER OF COULOMBS FOR REDUCTION OF THE FILM ON PASSIVE GOLD.

HCl (<i>N</i>).	Current Density.		Millicoulombs for Reduction.
	Passivating.	Reducing.	
0.125	0.014	0.008	0.98
0.125	0.035	0.008	1.14
0.125	0.021	0.006	0.86
0.25	0.053	0.008	1.18

The quantity of electricity required for reduction appears to be reasonably constant, even under the varying conditions of the experiments.

When gold is made anode in a solution of sulphuric acid, owing to the insolubility of gold in H_2SO_4 , oxygen is readily evolved, and a film of oxide is formed on the surface of the electrode. It would be expected that, on taking a fresh gold anode, the development of the full oxygen overvoltage might be delayed until the surface of the electrode was completely covered by the oxide layer. The quantity of electricity required to form the film should be independent of the current density used, and of the concentration of H_2SO_4 . In measuring the changes occurring, the circuit shown in Fig. 1 was slightly modified. The commutator slip rings were connected to a 72 volt battery, while the other brushes were connected to the anode and cathode. On rotating the commutator, the electrode was made alternately anode and cathode. In a solution of 2 *N* H_2SO_4 a fresh electrode, with a current density of 0.0037 amps./cm.² showed a break lasting for about 0.5 sec. before attaining the full oxygen overvoltage. The oxide film formed was quite stable, and even after insulating the electrode for some considerable time, no further break in the voltage curve was observable on switching on the current. Treatment with hydrochloric acid or cathodic reduction both restored the electrode to its initial state. On continued treatment of the electrode as an anode, the oxide film increased in thickness and eventually attained visible dimensions. The time required for the reduction of the film depends on its size, so that a measurement of the amount of current passed before the commencement of the evolution of H_2 would also serve to indicate the thickness of the film. Table VIII shows the amount of electricity required to form a film, and also to reduce it in solutions of 2.0 *N* and 21 *N* H_2SO_4 . All time measurements were taken from oscillograms of the voltage of the electrode against normal calomel. It will be observed that the quantity of electricity required for reduction

TABLE VIII.

Conc. of H_2SO_4	C.D. m.a./cm. ²	Coulombs for Reduction $\times 10^{-2}$ /cm. ²	Coulombs for Formation $\times 10^{-2}$ /cm. ²
2.0 N	3.74	2.94	2.37
2.0 N	8.31	3.54	2.27
21.0 N	4.10	1.71	1.90

is in general greater than that required for the formation of the film, this is due to increase in the thickness during the further passage of current subsequent to the completion of the film.

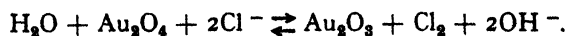
By assuming that the spacing of the centres of the gold atoms is the same in the film as in the metal, and that in the metal the atoms are arranged with their centres in the manner of a cubic pile of shot, the thickness of the film of auric oxide formed in H_2SO_4 can readily be calculated. The above calculation leads to values ranging from 7.9 molecules to 9.8 mols. for the thickness of the auric oxide film. If it be assumed that the passive state in HCl solutions is characterised by a film of Au_2O_3 , then values of 2.6 and 3.6 molecules are obtained for the thickness.

The values obtained above for the thickness are not exact, since in all cases the surface of the electrode is not a perfect plane, but possesses a visible crystalline structure. For all practical purposes, however, the film can be considered as only mono- or bimolecular, in both H_2SO_4 and HCl.

Discussion of Results.

Most modern theories of passivity postulate the existence of some sort of a protective film over the surface of the passive metal, and the above results are in no way in contradiction to such a view. That the film on an anodically passivated metal does not consist of a salt or basic salt, readily soluble as such in the electrolyte, seems to be proved by two well-known experimental facts, now once again observed in the course of this work. These are, first, that an extremely small current is sufficient to maintain the passive state and, second, that a high back E.M.F. persists after the passivating current has been cut off, as could not be the case were the high voltage characterising passivity merely the result of an ohmic resistance across the surface film.

Without any claim to originality, the following considerations of the structure and reactions of a passive gold anode are offered as providing a mechanism which satisfactorily explains all the experimental observations outlined above. The surface of the passive electrode is coated with a film which consists at first of gold atoms in some high state of oxidation. For convenience the film, at this stage, is considered to be gold peroxide, although it is, of course, impossible to suggest any precise composition. The peroxide is not directly soluble in acid, but it can react with chloride ion and water to produce chlorine and a lower oxide by some such reaction as



The suggestion of reversibility is based on the observed increase in the time of recovery with any change in conditions which cause an increase

in concentration of chlorine around the electrode. Saturation of the electrolyte with chlorine, increase in current density on the passive electrode, or decrease in the rate of stirring, each cause a fall in the velocity of reactivation. Such a mechanism demands that the rate of recovery should be proportional to the square of the concentration of chloride ion and, within the limitations of the method, this is in agreement with the experimental results obtained. The auric oxide is subsequently dissolved. The rate of solution should be proportional to the activity or concentration of the hydrogen ion, and this point of view also is born out by the results. The thickness of the film has been shown above to be not more than one or two molecular layers.

The form of the recovery curve (Fig. 2) may now be explained in terms of these views. On breaking the passivating circuit the peroxide on the face of the anode at once reacts with the chloride in solution and chlorine is evolved, the equilibrium pressure of the latter, under the experimental conditions employed, being above one atmosphere. This reaction continues undisturbed until the point C is reached. During the period represented by AC the auric oxide resulting from the breakdown of the peroxide has been attacked by the acid and, by the end of this time, holes are beginning to appear in the film. If the peroxide be supposed to be analogous to the lead peroxide on an accumulator plate and shows similar electromotive activity, then the appearance of holes in the film brings in a new source of loss of peroxide. The film of higher oxide and metallic gold form a short-circuited cell. The peroxide decomposes and the exposed atoms of gold are oxidised (ionised) and pass into solution. Under these conditions, the peroxide disappears by the two reactions and chlorine is not produced as rapidly as it is removed by diffusion into the stirred electrolyte. The potential falls steadily until the point D is reached and the last traces of peroxide have gone. Any residue of auric oxide is quickly dissolved and the potential falls to that of active gold at B. Before perforation of the film the passive anode is considered to behave as a chlorine electrode at one atmosphere pressure or slightly more. Within the accuracy of measurement of potentials from oscillograms, this assumption is supported by experiment, as is shown by the following figures:—

[Cl ⁻]	eCl (volts).	
	Calc.	Obs.
0.5	1.384	1.39
0.75	1.373	1.38

It is noteworthy that the potential of active gold in *N* HCl through which chlorine is bubbled falls approximately on the portion of the recovery curve represented by CD.

The heterogeneous nature of the system and the complexity of the processes involved make exact calculations of the reaction kinetics as yet impossible; it is evident, however, that the mechanism postulated demands that the rate of production of chlorine from loss of peroxide and chloride shall be proportional to the square of the chloride ion concentration and that the solution of the lower oxide shall be governed by the concentration of acid immediately in contact with the electrode. The experiments on cathodic reduction of the film have shown the thickness to be a constant for concentrations of HCl up to 0.25 *N* and it may be postulated, from the general nature of the results, that the film has the same dimensions over the whole range of conditions employed.

With this assumption, the rate of reaction may be taken as the reciprocal of the time involved. Thus in constant chloride solution the total time of recovery should be made up of two factors, the first, representing the time required for interaction between peroxide and chloride (approximately constant and consisting mainly of the period between commencement of recovery and perforation of the film) and the second, the time taken in solution of the oxide. This is in accordance with the result

that $\theta = \frac{K}{[H^+]} + \theta_{Cl}$, where θ_{Cl} remains constant for any one concentration of chloride. It is noteworthy that K , which may be taken as the time required for solution of the auric oxide in unit concentration of acid, alters little with change in concentration of chloride. This is evidenced by the similarity in slope of the lines in Fig. 3. Owing to the loss of peroxide by a second reaction, which sets in as soon as exposed gold appears, it is too much to expect that any exact relation can be shown between θ_{Cl} and the chloride-ion concentration. Nevertheless, when θ

is extrapolated to $\frac{1}{[H^+]} = 0$, so that $\theta = \theta_{Cl}$, there is a rough approximation to proportionality between the time of recovery and the square of the chloride concentration. Exact proportionality might be expected only if the whole of the peroxide disappeared solely by formation of chlorine.

It has been possible to obtain some further experimental evidence for this interpretation of the quantity θ_{Cl} by use of the method of applying an extremely small current to the electrode at times corresponding to various points on the recovery curve (Fig. 2). The duration of full passivity has been measured in solutions containing varying quantities of hydrogen and chloride ions by observing the moment at which the application of a few milliamperes ceased to produce an instantaneous rise of potential to the value characterising the passive state. As explained above, this period of full passivity corresponds to the length AC. The following figures were obtained for three concentrations of hydrogen ion and two of chloride:—

Electrolyte.	AC (Seconds).	
	S.	D.
1.0 HCl	0.38	0.54
0.5 HCl + 0.5 HCl	0.40	0.57
0.75 HCl	0.91	1.12

It will be observed that the value of AC, which is considered to be only slightly less than θ_{Cl} , varies little with acid concentration so long as the content of chloride ion remains constant; with decrease in the latter, however, the period of complete passivity increases rapidly; in fact, its rate of increase is much the same as that of values of θ_{Cl} obtained by extrapolation of θ to infinite concentration of hydrogen ion. The comparatively small, but definite, decrease in AC with increase in acid (at constant chloride) might be ascribed to an increased rate of solution of lower oxide formed by the breaking down of the peroxide layer.

Thus it must be concluded that the first reaction in the recovery process is one independent of acid content but proceeding at a rate proportional to some power approximating to the square of the chloride-ion concentration; the subsequent reaction is one involving the solution of auric oxide at a velocity directly governed by the hydrogen ion.

Summary.

The fall in potential during the spontaneous reactivation of a passivated gold anode has been examined under conditions which do not permit of direct electrical depolarisation, and the total time required for the recovery of the active form has been determined in acid chloride solutions.

The effect of temperature on the rate of recovery has been studied. The high temperature coefficient obtained suggests that the rate of the recovery process is controlled by a chemical reaction distinct from simple solution of the film and diffusion of the products.

Cathodic reduction of an anode passivated in chloride solution has shown the film on the electrode to be not more than one or two molecular layers in thickness. Some measurements of film thickness have also been made in sulphuric acid solutions.

The experimental data have been shown to lead to the conclusion that the film consists initially of some higher oxide, to which is ascribed the high potential characterising passivity. After the passivating current has been cut off, this peroxide reacts with chloride to produce chlorine and auric oxide, the latter subsequently dissolving in acid solution.

*The Muspratt Laboratory of Physical and Electrochemistry,
University of Liverpool.*

THE KINETICS OF THE IODINE-OXALATE REACTION.

BY ROBERT OWEN GRIFFITH AND ANDREW MCKEOWN.

Received 26th July, 1932.

In recent papers we have shown that the thermal oxidation of oxalates by bromine¹ and by chlorine² follows the kinetic law :

$$\text{rate} \propto \frac{1}{[X^-]\{K_3 + [X^-]\}} \cdot \frac{[\text{HC}_2\text{O}_4^-]}{[\text{H}^+]} \cdot [\Sigma X_2],$$

where X is the halogen, $[\Sigma X_2]$ is the concentration of titratable halogen, and $K_3 = [X_2][X^-]/[X_3^-]$. From this it was inferred that the rate-determining process is a reaction between the hypohalous acid HOX formed by hydrolysis of the halogen and the HC_2O_4^- ion. It seemed to be of interest to investigate whether the thermal reaction between iodine and oxalates has the same mechanism. Since the published data on this reaction are somewhat scanty, we have therefore carried out a series of fresh measurements, the results of which are now communicated.

The oxidation of oxalates by iodine has previously been studied by Dhar³ and by Berthoud and Bellenot.⁴ The latter workers found the rate to be proportional to the concentration of titratable iodine and to the concentration of oxalate, but inversely proportional to the concentration of potassium iodide. Further, the reaction has a very high temperature coefficient: Berthoud and Bellenot give $k_{70}/k_6 = 4.36$ between 66° and 78°, in agreement with Dhar's values of 5.4 between

¹ Griffith, McKeown and Winn, *Trans. Faraday Soc.*, **28**, 107, 1932.

² Griffith and McKeown, *Trans. Faraday Soc.*, **28**, 518, 616, 1932.

³ Dhar, *J.C.S.*, **111**, 690, 1917.

⁴ Berthoud and Bellenot, *J. Chim. phys.*, **21**, 308, 1924.

50° and 60°, 6.1 between 40° and 50°, and 7.2 between 25° and 40°. However, more recent observations of Berthoud⁵ do not appear to have confirmed the original conclusions of Berthoud and Bellenot; the velocity is now stated to be approximately proportional to the concentration of oxalate and to the *square root* of the concentration of iodine. From this it is inferred that this thermal reaction has the same mechanism as the corresponding photochemical reaction, that is, a mechanism involving iodine atoms. Berthoud's experimental data, from which this conclusion is drawn, have not yet been published, so that it is not possible to judge how far his results are in accord with ours.

The data which we ourselves have obtained lead us to the view that the thermal oxidation is one in which *two* quite independent reactions are simultaneously operative. These two processes are:—

(a) a reaction between iodine atoms and oxalate ions, as already found by Berthoud;

(b) a reaction between HOI and HC_2O_4^- ions, analogous to the chlorine and bromine-oxalate cases already studied. These follow from the kinetic equation which is found to fit the experimental results:—

$$\begin{aligned}\frac{dx}{dt} &= k_{1/2} \cdot [\text{C}_2\text{O}_4^{--}] \sqrt{\frac{\Sigma \text{I}_2}{K_3 + [\text{I}^-]}} + k_1 [\text{C}_2\text{O}_4^{--}] \cdot \frac{\Sigma \text{I}_2}{[\text{I}^-] \{K_3 + [\text{I}^-]\}} \\ &= [\text{C}_2\text{O}_4^{--}] \left\{ k_{1/2} \frac{\sqrt{\Sigma \text{I}_2}}{\sqrt{K_3 + [\text{I}^-]}} + k_1 \frac{\Sigma \text{I}_2}{[\text{I}^-] \{K_3 + [\text{I}^-]\}} \right\},\end{aligned}$$

where $k_{1/2}$ is a semi-molecular constant, k_1 a unimolecular constant, ΣI_2 is the concentration of titratable iodine, and K_3 is the equilibrium constant of tri-iodide formation. Though it has not been possible to integrate this equation for the chosen experimental conditions, a satisfactory demonstration that the reaction does obey a kinetic law of this complex character has, we consider, been effected.

Experimental.

The oxalates, iodine and potassium iodide used were A.R. preparations. Conveniently measured rates of reaction are obtained in the temperature range 40° to 60° C., and since oxalate solutions slowly attack glass at these temperatures, the experiments were carried out in stoppered quartz flasks of about 300 c.c. capacity. Special precautions were taken to exclude all light from the reacting system. The change with time of titratable iodine was followed by running samples of the reaction mixture into excess of a standard sodium arsenite solution and back titrating with standard iodine. In all experiments the concentration of the oxalate ($M/12 - M/6$) was so much greater than that of the iodine ($M/100 - M/1500$) that it could be regarded as constant throughout the course of reaction. The initial concentration of potassium iodide was varied between $M/5$ and $M/1000$. All concentrations are given in gram-molecules per litre at 15° C.

Reaction Kinetics and Experimental Results.

The experimental data may conveniently be divided into two categories: (a) experiments in which the semimolecular reaction predominates; (b) experiments in which the semimolecular and the

⁵ Berthoud, *Trans. Faraday Soc.*, **27**, 527, 1931 (General Discussion on "Photochemical Processes"; Liverpool, April, 1931).

754 THE KINETICS OF THE IODINE-OXALATE REACTION

unimolecular reactions contribute comparable amounts to the whole. Examination of the complete kinetic equation given above shows that the favourable condition for predominance of the semimolecular process is a high concentration of the iodide ion. Actually we find that in a solution of $\frac{M}{10}\text{KI} + \frac{M}{100}\text{I}_2$ or $\frac{M}{20}\text{KI} + \frac{M}{250}\text{I}_2$ the unimolecular process is almost completely suppressed. The so isolated semimolecular component may now be examined from the standpoint of its dependence upon the concentrations of oxalate, iodine, and potassium iodide. First, the order of reaction with respect to iodine has been tested by comparing two experiments with the same (high) concentrations of oxalate and of potassium iodide but different initial concentrations of iodine. The results of several comparisons of this character are summarised under expts. 1, 1a to 5, 5a in Table I. The k_{semi} 's of the fifth column are calculated from the integrated form of the simple semimolecular equation

$$-\frac{d(a-x)}{dt} = k_{\text{semi}}(a-x)^{1/2},$$

$$\text{viz.} \quad k_{\text{semi}} = \frac{2}{t}\{a^{1/2} - (a-x)^{1/2}\}.$$

The k_{uni} 's of the sixth column are derived from

$$k_{\text{uni}} = \frac{1}{t} \log_e \frac{a}{a-x},$$

where a and $a-x$ represent the concentrations of titratable iodine initially and at time t (min.).

TABLE I.

Expt. No.	Temp.	[Oxalate].	[KI].	$[\Sigma \text{I}_2]_{\text{init.}}$	$k_{\text{semi}} \times 10^6$.	$k_{\text{uni}} \times 10^6$.	$k_{1/2} \times 10^6$.
{ 1 1a	60°	M/6 $\text{K}_2\text{C}_2\text{O}_4$	M/10	M/200 M/1000	165 162	254 658	312 311
{ 2 2a	55°	M/6 $\text{K}_2\text{C}_2\text{O}_4$	M/10	M/200 M/1000	70.8 73.2	104 243	133 140
{ 3 3a	55°	M/6 $\text{Na}_2\text{C}_2\text{O}_4$	M/10	M/100 M/400	65.7 64.7	69.6 141	121 123
{ 4 4a	45°	M/6 $\text{Na}_2\text{C}_2\text{O}_4$	M/10	M/100 M/400	11.1 10.6	12.2 23.4	20.7 20.1
{ 5 5a	45°	M/6 $\text{Na}_2\text{C}_2\text{O}_4$	M/20	M/250 M/1000	15.7 14.8	26.9 55.0	21.0 20.1
6	45°	M/12 $\text{Na}_2\text{C}_2\text{O}_4$	M/10	M/400	5.74	—	21.8
7	45°	M/6 $\text{Na}_2\text{C}_2\text{O}_4$	M/5	M/400	7.64	—	20.6
8	50°	M/6 $\text{Na}_2\text{C}_2\text{O}_4$	M/10	M/400	26.8	—	50.8
9	40°	M/6 $\text{Na}_2\text{C}_2\text{O}_4$	M/10	M/400	4.25	—	8.1

In each pair of experiments the time interval from the start was the same, so that obedience to the unimolecular law would have entailed the same fractional loss of iodine for the two different initial concentrations of iodine. This, however, was very far from being the case, as is shown by the very decided differences in the k_{uni} 's for each pair. On the other hand, the k_{semi} 's for four and five-fold changes in $[\Sigma \text{I}_2]_{\text{init.}}$ are in very fair accord with one another, leaving no room for doubt as to the semimolecular nature of the process involved.

Experiments 4a and 6 show the effect of doubling the concentration of oxalate upon the rate of this semimolecular process. The first k_{semi} is practically twice the other, so that we may assume the order of reaction with respect to oxalate to be unity. Actually, the ionic strengths of these solutions are rather high, and the value of the "constant" when allowance is made for the change in the concentration of oxalate may still be a function of the ionic strength of the reaction mixture. That specific ionic strength effects are present is suggested by a comparison of experiments 2, 2a and 3, 3a. The k_{semi} with potassium oxalate is distinctly higher than that with sodium oxalate at the same concentration. To avoid difficulties due to such effects, we have used sodium oxalate alone at a constant initial concentration of $M/6$ in all subsequent experiments.

Finally, experiments 4, 4a, 5, 5a and 7 are designed to illustrate the dependence of k_{semi} upon the iodide content. It will be seen that a four-fold increase in the concentration of potassium iodide (from $M/20$ to $M/5$) has practically halved the rate of reaction. This naturally suggests a kinetic equation with the rate of the semimolecular process inversely proportional to the square root of iodide concentration, or perhaps to the square root of iodide concentration plus a constant, the latter small compared with the concentrations of iodide used in these test experiments. For reasons which will appear later, the kinetic equation which we favour is:

$$\frac{dx}{dt} = k_{1/2} \cdot [\text{C}_2\text{O}_4^{--}] \cdot \frac{\sqrt{\Sigma \text{I}_2}}{\sqrt{K_3 + [\text{I}^-]}}$$

and the $k_{1/2}$'s of the last column of Table I are computed on this basis. The values of K_3 used in the calculations are 1.75, 1.88, 2.02, 2.16 and 2.30×10^{-3} at 40°, 45°, 50°, 55° and 60°, these being based on the mean value $K_3 = 1.39 \times 10^{-3}$ at 25° of a large number of workers and Fedotieff's value⁶ of 1.75×10^{-3} at 40° C.

Turning now to experiments with low concentrations of potassium iodide ($M/160$ and less), examination of the data at once showed that the kinetic law which holds for high concentrations now breaks down. This showed itself in various ways. For example, the initial $k_{1/2}$ is considerably greater than the values given above; in a reaction mixture with $M/6 \text{ Na}_2\text{C}_2\text{O}_4 + M/160 \text{ KI} + M/1000 \text{ I}_2$ at 45° C. the initial $k_{1/2}$ is practically double the value of 20.7×10^{-6} which should obtain according to Table I. This disparity increases with diminishing concentration of potassium iodide, so that with $M/1000 \text{ KI}$ and other conditions as before, the initial $k_{1/2}$ is between three and four times the true value. Furthermore, in each experiment with a low concentration of potassium iodide $k_{1/2}$ falls with time, that is, with decreasing concentration of iodine and increasing concentration of iodide ion. These facts suggest that another simultaneous mode of reaction between iodine and oxalate, which is more strongly retarded by I^- ion and is therefore practically completely inhibited at high concentrations of iodide, is now contributing an appreciable amount to the measured rate of reaction. The process which naturally suggested itself to us in this connection is an oxidation of oxalate by iodine following a mechanism analogous to that already demonstrated in the cases of chlorine and bromine, *viz.* reaction between HOI and the HC_2O_4^- ion. The rate of this reaction is proportional

⁶ Fedotieff, *Z. anorg. Chem.*, **69**, 91, 1911.

756 THE KINETICS OF THE IODINE-OXALATE REACTION

to $[C_2O_4^{--}]$ and to ΣI_2 , but the retardation by I^- ion is proportional to the product $[I^-]\{K_3 + [I^-]\}$. The whole reaction as measured should then follow the kinetic law:

$$\frac{dx}{dt} = [C_2O_4^{--}] \left\{ k_{1/2} \frac{\sqrt{\Sigma I_2}}{\sqrt{K_3 + [I^-]}} + k_1 \frac{\Sigma I_2}{[I^-]\{K_3 + [I^-]\}} \right\}.$$

We have tested this equation by means of our experimental data, and, as already stated, find that it is in satisfactory agreement.

With low iodide concentrations, the value of $[I^-]$ increases considerably with time in each experiment, and, though $[I^-]$ is approximately a linear function of x , the above equation assumes a non-integrable form. We have therefore had to employ the method of finite differences, with the kinetic equation written in the form:

$$-\frac{\Delta(\Sigma I_2)}{\Delta t} = \frac{\Delta x}{\Delta t} = [C_2O_4^{--}] \cdot \left\{ k_{1/2} \frac{\sqrt{\Sigma I_2(m)}}{\sqrt{K_3 + [I^-](m)}} + k_1 \frac{\Sigma I_2(m)}{[I^-](m)\{K_3 + [I^-](m)\}} \right\}.$$

Here, Δx = moles per litre of iodine transformed in the time interval Δt (min.), and $\Sigma I_2(m)$ and $[I^-](m)$ are the mean concentrations of titratable iodine and of free iodide ion in the time interval. The concentrations of free iodide ion at various stages of an experiment are obtained from the relation (*cf.* ref. (1), p. 111):

$$[I^-]_t = \frac{1}{2} \{c - a - K_3 + 3x + \sqrt{(c - a - K_3 + 3x)^2 + 4K_3(c + 2x)}\},$$

in which c = initial concentration of total iodide, $a = \Sigma I_2$ (initial), and $a - x = \Sigma I_2$ at time t . The method of procedure then followed may be illustrated by considering two typical experiments (Tables II and III).

TABLE II.

$$\frac{M}{6} Na_2C_2O_4 + \frac{M}{320} KI + \frac{M}{750} \text{ (approx.) } I_2. \quad \text{Temp.} = 50^\circ C.$$

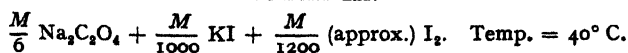
ΣI_2 , $\times 10^4$.	$[I^-]$, $\times 10^3$.	Δt .	$\Sigma I_2(m)$, $\times 10^4$.	$[I^-](m)$, $\times 10^3$.	$\Delta(\Sigma I_2)_{(tot.)}$, $\times 10^4$.	$\Delta(\Sigma I_2)_{(semi)}$, $\times 10^4$.	$\Delta(\Sigma I_2)_{(uni)}$, $\times 10^4$.	k_1 , $\times 10^8$.
12.19	2.585	19.95	11.22	2.812	1.940	0.810	1.130	41.3
10.25	3.040	26.25	9.294	3.274	1.911	0.927	0.984	42.2
8.339	3.508	36.95	7.389	3.748	1.900	1.115	0.785	37.6
6.439	3.989	46.35	5.531	4.224	1.815	1.164	0.651	40.5
4.624	4.460	67.53	3.709	4.703	1.830	1.338	0.492	37.5
2.794	4.946							

Mean value of $k_1 \times 10^8 = 39.8$

The $\Delta(\Sigma I_2)_{(tot.)}$ of the sixth column of these tables corresponding to the time interval Δt requires to be apportioned between the semi-molecular process and the simultaneous unimolecular process. In computing the semimolecular contribution $\Delta(\Sigma I_2)_{(semi)}$ for each time interval, the value of $k_{1/2}$ in the relation

$$\Delta(\Sigma I_2)_{(semi)} = k_{1/2} [C_2O_4^{--}] \cdot \frac{\sqrt{\Sigma I_2(m)}}{\sqrt{K_3 + [I^-](m)}} \cdot \Delta t$$

TABLE III.



ΣI_2 $\times 10^4$	$[\text{I}^-]$ $\times 10^4$	Δt	$\Sigma \text{I}_2(m)$ $\times 10^4$	$[\text{I}^-](m)$ $\times 10^4$	$\Delta(\Sigma \text{I}_2)(\text{tot.})$ $\times 10^4$	$\Delta(\Sigma \text{I}_2)(\text{semi})$ $\times 10^4$	$\Delta(\Sigma \text{I}_2)(\text{uni})$ $\times 10^4$	k_1 $\times 10^8$
8.119	0.811	51.97	7.400	0.954	1.437	0.3643	1.0727	4.32
6.682	1.098	66.88	6.092	1.227	1.179	0.4053	0.7737	4.18
5.503	1.357	92.20	4.934	1.483	1.138	0.4827	0.6553	4.15
4.365	1.610	141.25	3.751	1.756	1.227	0.6190	0.6080	4.24
3.138	1.902							

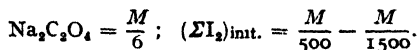
Mean value of $k_1 \times 10^8 = 4.22$

is the value obtained in the experiments with high iodide concentrations and given in Table I, *viz.* 8.1×10^{-6} and 50.8×10^{-6} at 40° and 50° respectively. Subtracting the figures of column (7) from those of column (6) gives the values $\Delta(\Sigma \text{I}_2)(\text{uni})$ of column (8), from which the unimolecular constant k_1 is then calculated by means of the equation

$$k_1 = \frac{\Delta(\Sigma \text{I}_2)(\text{uni})}{\Delta t} \cdot \frac{1}{[\text{C}_2\text{O}_4^{--}]} \cdot \frac{[\text{I}^-](m) \{K_3 + [\text{I}^-](m)\}}{(\Sigma \text{I}_2)(m)}$$

It will be seen that, having regard for the mode of calculation, k_1 is reasonably constant in each experiment. The postulated mechanism is, however, further substantiated by the results of Table IV, which summarises all our kinetic measurements with low concentrations of iodide. Calculated by the method described above, each value of k_1 in this Table is the mean of the four or five values resulting from each experiment. It will be observed that at each temperature the same value of k_1 is obtained from experiments with different initial concentrations of the retarding iodide ion, which involves considerable variations in the ratio $\Delta(\Sigma \text{I}_2)(\text{semi})/\Delta(\Sigma \text{I}_2)(\text{uni})$.

TABLE IV.



Temp. = 40° . $k_{1/2} = 8.1 \times 10^{-6}$.		Temp. = 45° . $k_{1/2} = 20.7 \times 10^{-6}$.		Temp. = 50° . $k_{1/2} = 50.8 \times 10^{-6}$.	
[KI] init.	$k_1 \times 10^8$	[KI] init.	$k_1 \times 10^8$	[KI] init.	$k_1 \times 10^8$
$M/1000$	4.22	$M/1000$	13.7	—	—
$M/640$	4.28	$M/640$	14.0	$M/640$	40.9
$M/320$	4.26	$M/320$	13.5	$M/320$	39.8
—	—	$M/160$	14.1	$M/160$	39.1

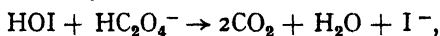
The constancy of k_1 at each temperature supports strongly not only the kinetic equation adopted for the unimolecular part of the reaction, but also that which we have used to represent the semimolecular fraction.

It will be recalled that at the high iodide concentrations necessary to isolate the semimolecular process, it is impossible to distinguish between an iodide retardation proportional to $\sqrt{[I^-]}$ and one proportional to $\sqrt{K_3 + [I^-]}$. Now, however, if the rate of the semimolecular process is assumed inversely proportional to $\sqrt{[I^-]}$, the resulting k_1 in the experiments of Table IV is constant neither within each experiment nor from experiment to experiment. Certainly, an additive constant of the order of magnitude of K_3 seems to be required under the square root in the denominator, and since, further, a semimolecular reaction with a velocity inversely proportional to $\sqrt{K_3 + [I^-]}$ is capable of a simple theoretical interpretation, we may regard this form of iodide retardation to be as satisfactorily established as circumstances permit.

Discussion.

Accepting our interpretation of the experimental data, the thermal reaction between $\text{Na}_2\text{C}_2\text{O}_4$ and I_2 at temperatures between 40° and 60° occurs simultaneously by two entirely different processes, one semimolecular and the other unimolecular with respect to iodine, both retarded by iodide ions, the unimolecular process, however, more strongly. In the above temperature interval, with concentrations of iodine of the order of $M/1000$, and with iodide concentrations in the range $M/160$ to $M/1000$, both reactions occur with speeds of the same order of magnitude.

Discussing first the unimolecular process, whose rate, as already stated, is determined by the reaction



it has been shown (*cf.* Refs. (1) and (2)), that the observed unimolecular constant k_1 is equal to the function kK/K_3 , where k is the bimolecular velocity constant of the rate-determining reaction, K is the hydrolytic constant of iodine ($K = [\text{HOI}][\text{H}^+]/[\text{I}_2]$), K_3 is the equilibrium constant of tri-iodide formation ($K_3 = [\text{I}_2][\text{I}^-]/[\text{I}_3^-]$), and K_2 is the second ionisation constant of oxalic acid ($K_2 = [\text{H}^+][\text{C}_2\text{O}_4^{2-}]/[\text{HC}_2\text{O}_4^-]$).

The temperature coefficient of k_1 is an extraordinarily high one. From Table IV it is seen to amount to 9.4 between 40° and 50° , which corresponds to a critical increment (E) of 45,100 calories. To obtain the critical increment of the rate-determining reaction, we must subtract from this value 2850 cal. for the variation of K_3 , about 1000 cal. for the variation of K_2 (*cf.* Ref. (1), p. 122), and 22,700 cal. for the variation of the hydrolytic constant K with temperature. (The last of these values is derived from the figures $K = 3 \times 10^{-13}$ at $25^\circ \text{C}.$ ⁷ and $K = 9 \times 10^{-15}$ at $0^\circ \text{C}.$ ⁸). We thus arrive at the value $E = 18,550$ cal. as the critical increment of the reaction between HOI and HC_2O_4^- , which corresponds to a temperature coefficient of 3.08 between 10° and 20° , and of 2.51 between 40° and 50° . The reaction has thus a somewhat higher critical increment than those of the corresponding reactions of HOCl and HOBr , for both of which $E = 15,000$ cal.

The absolute value of k is also easily calculated. We have, for example at 45° , $k_1 = 13.8 \times 10^{-8}$. This refers to a solution of $M/6$ $\text{Na}_2\text{C}_2\text{O}_4$, for which the ionic strength (μ) is 0.5. We estimate that under these conditions $K_2 = 1.75 \times 10^{-4}$ and $K_3 = 1.88 \times 10^{-3}$.^{*} For

⁷ Bray, *J. Amer. Chem. Soc.*, **32**, 914, 1910.

⁸ Jones, *J. Amer. Chem. Soc.*, **37**, 24, 1915.

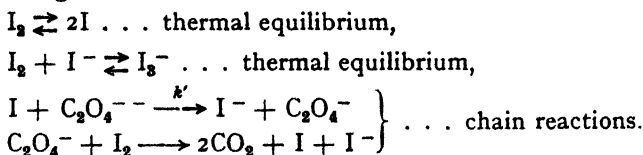
* No allowance for the effect of ionic strength on K_3 has been made.

K at $\mu = 0$ and a temperature of 45° we obtain 3.33×10^{-12} ; by analogy with the variations of the hydrolytic constants of chlorine and bromine with ionic strength (*cf.* Refs. (1) and (2)), we estimate that the above value of K increases to about 5.8×10^{-12} when $\mu = 0.5$. We then obtain

$$k = \frac{k_1 K_2}{K K_3} = \frac{13.8 \times 10^{-8} \times 1.75 \times 10^{-4}}{5.8 \times 10^{-12} \times 1.88 \times 10^{-3}} = 2000 \text{ (approx.)}$$

at 45° , or about 250 at 20° . The latter figure may be compared with the corresponding k for the $\text{HOCl} - \text{HC}_2\text{O}_4^-$ reaction of about 600, and with that for the HOBr reaction of about 16500 at the same temperature.

Turning now to the semimolecular process, there appears to be little doubt that, as suggested by Berthoud,⁵ this must involve reaction between iodine atoms and $\text{C}_2\text{O}_4^{--}$ ions. The simplest possible interpretation on this basis of the kinetic law which the semimolecular process obeys is the following reaction mechanism:—



These chain reactions are identical with those originally suggested by Berthoud and Bellenot⁴ for the *photo-oxidation* of $\text{K}_2\text{C}_2\text{O}_4$ by I_2 . Writing $K_0 = [\text{I}]^2/[\text{I}_2]$, and $K_3 = [\text{I}_2][\text{I}^-]/[\text{I}_3^-]$, the stationary concentration of iodine atoms is given by

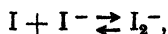
$$[\text{I}] = \sqrt{K_0[\text{I}_2]} = \sqrt{\frac{K_0 K_3 (\Sigma \text{I}_2)}{K_3 + [\text{I}^-]}}$$

and the rate of reaction by

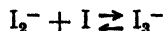
$$-\frac{d[\text{C}_2\text{O}_4^{--}]}{dt} = k' \cdot [\text{C}_2\text{O}_4^{--}] \cdot \sqrt{\frac{K_0 K_3 (\Sigma \text{I}_2)}{K_3 + [\text{I}^-]}}$$

in formal agreement with the kinetic law to which our experiments conform.

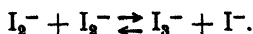
While the above represents the simplest interpretation of the semimolecular process, it is capable of a variety of modifications. For example, there may enter the equilibrium



involving the ion I_2^- , whose existence has been postulated by a number of workers,⁹ together with such processes as



and



Provided, however, that thermodynamic equilibrium holds for each of the reversible reactions postulated, their existence cannot affect the final result so long as the rate-determining reaction is one between iodine atoms and oxalate ions. We have nevertheless mentioned the possible intervention of I_2^- in the present case, since in the *photochemical* re-

⁹ Wagner, *Z. physikal. Chem.*, **113**, 261, 1924; Dickinson and Ravitz, *J. Amer. Chem. Soc.*, **52**, 4770, 1930; Allmand and Young, *Trans. Faraday Soc.*, **27**, 515, 1931.

actions between iodine (and bromine) and oxalates, which we are now reinvestigating, I_2^- (and Br_2^-) ions appear to play important rôles.

Identifying the semimolecular constant $k_{1/2}$ with $k'\sqrt{K_0K_3}$, it is possible to calculate—at least approximately—the temperature coefficient and critical increment E' of k' . From Table I it is seen that $k_{1/2}$ has the temperature coefficients (per 5°) 2.56, 2.45, and 2.40 between 40° and 45°, 45° and 50°, and 50° and 55° respectively. These yield critical increments of the measured reaction of 37,200, 36,700, and 37,000 calories, giving a mean of 37,000 calories. Assuming now that the heat of dissociation of molecular iodine into atoms has the same value in aqueous solution as in the gaseous state, namely 35,600 calories,¹⁰ we have to subtract half this heat of dissociation plus half the heat of dissociation of KI_3 from the observed critical increment to obtain that of k' . We thus find $E' = 37,000 - (17,800 + 1400) = 17,800$ calories. This would correspond to a temperature coefficient between 40° and 50° of 2.42 for the reaction between iodine atoms and $C_2O_4^{--}$ ions.

Only a very rough estimate of the absolute value of k' is possible, owing to the fact that a very extended extrapolation of the equilibrium data for the thermal dissociation of iodine into atoms must be made, and even then the resulting value of K_0 refers to the gaseous state and not to dissociation in aqueous solution. Application of the formula of Braune and Ramst tter¹¹ for the variation of the gaseous equilibrium with temperature yields $K_0 = 3.7 \times 10^{-21}$ at 45° C., while the formula of de Vries and Rodebush¹² gives $K_0 = 4.9 \times 10^{-20}$ at the same temperature. On the one basis k' at 45° works out to 7×10^6 , on the other to 2×10^6 , the units being litres/moles-minutes.

Finally, it might be mentioned that we have attempted without success to obtain evidence of a reaction between iodine atoms and $HC_2O_4^-$ ions. In an experiment with a solution containing $NaHC_2O_4$, iodine, and potassium iodide, the observed small extent of reaction could be accounted for entirely in terms of the reaction between the $HC_2O_4^-$ ion and HOI and of that between iodine atoms and the small amount of $C_2O_4^{--}$ ions present as a result of the slight dissociation of the $HC_2O_4^-$ ions. If a reaction between $HC_2O_4^-$ and I does occur, we estimate that its specific rate is not greater than 2 per cent. of that of the reaction between $C_2O_4^{--}$ and I.

Summary.

The thermal reaction $Na_2C_2O_4 + I_2 \rightarrow 2NaI + 2CO_2$ in aqueous solution has been studied in the temperature range 40° to 60°, and over a range of iodide concentration from $M/5$ to $M/1000$. The measured reaction is composite of two simultaneous and independent processes, the one unimolecular, the other semimolecular with respect to iodine. The first of these is interpreted as a reaction between $HC_2O_4^-$ and HOI, the other as a reaction between $C_2O_4^{--}$ and iodine atoms. The velocity constants and the critical increments of these two reactions have been evaluated.

The authors desire to express their indebtedness to Imperial Chemical Industries, Ltd., for a grant defraying part of the cost of this work.

*Muspratt Laboratory of Physical and Electrochemistry,
University of Liverpool.*

¹⁰ Gibson and Heitler, *Z. Physik*, **49**, 471, 1928.

¹¹ Braune and Ramst tter, *Z. physikal. Chem.*, **102**, 480, 1922.

¹² de Vries and Rodebush, *J. Amer. Chem. Soc.*, **49**, 656, 1927.

THE HEATS OF ADSORPTION OF HYDROGEN AND CARBON MONOXIDE ON COPPER.

BY RALPH A. BEEBE.

(*Contribution from Laboratory of Physical Chemistry, Bristol University.*)

Received 2nd August, 1932.

It is well known that there is lack of agreement in the experimental measurements of heats of adsorption on copper surfaces. Taylor and Kistiakowsky¹ measured the differential heats for hydrogen on copper with a platinum resistance thermometer and found low initial values which rose to a maximum after 1 to 2 c.c. of gas had been adsorbed. Ward,² using a multiple thermocouple external to the catalyst chamber, found that, for a given sample of copper, the heat of adsorption was independent of the amount of hydrogen already on the surface, although the value decreased greatly when the activity of the catalyst was diminished by sintering. In the case of carbon monoxide, Beebe³ found initial high heats which fell off rapidly to a much lower constant value after 2 to 3 c.c. had been adsorbed. Taylor and Kistiakowsky¹ obtained an S-shaped curve by plotting their experimental values of adsorption heats against the amount of carbon monoxide already on the surface.

This disagreement in the experimental data leads to a suspicion of faults in the experimental methods. Schwab and Brenneke⁴ have indicated that the low initial heats observed by Taylor and Kistiakowsky may be accounted for by defects in the resistance thermometer method resulting from the slow rate at which thermal equilibrium was established. So far as the author is aware, no explanation has been offered of the discordant results for carbon monoxide. Therefore a further study of the problem seemed desirable, especially over the low pressure range of initial adsorption where the discordant results had been found.

Experimental.

The copper adsorbent was prepared by reduction of high grade copper oxide granules in a stream of pure, dry hydrogen, first at 115° C. and finally at 140° C. as recommended by Benton.⁵ The 78 grams of this copper used adsorbed 2.10 c.c. of hydrogen and 8.0 c.c. of carbon monoxide at 3 mm. residual pressure. Between runs, the catalyst was evacuated at 150° C. All gases were carefully purified.

The general method chosen was very similar to that described by Garner and Kingman,⁶ except for the calorimeter proper, shown in Fig. 1. The design of this calorimeter was like that used by Beebe and Taylor⁷ but with the important difference that a single copper-constantan thermocouple was substituted for the Beckmann thermometer. It

¹ *Z. physik. Chem.*, **75**, 341, 1927.

² *J. Physic. Chem.*, **30**, 1538, 1926.

³ *Trans. Far. Soc.*, **28**, 1932.

⁴ *J. Amer. Chem. Soc.*, **46**, 43, 1924.

⁵ *Proc. Roy. Soc.*, **133A**, 506, 1931.

⁶ *Z. physik. Chem.*, **16B**, 19, 1932.

⁷ *Ibid.*, **27**, 322, 1931.

was possible to alter the position of the junction in the catalyst mass without dismantling the calorimeter. The "gas effect" mentioned

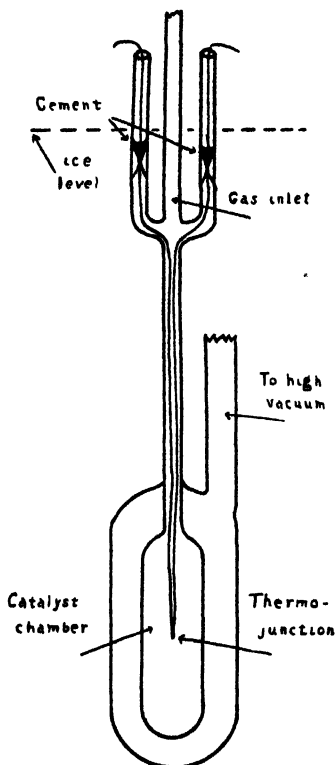


FIG. 1.

few per cent. and would apply equally to all the values of adsorption heats measured.

by Garner and Kingman was completely eliminated by keeping the level of the ice bath above the point where the leads from the thermo-junction emerged from the evacuated space. Because the only thermal contact with the outer bath was made along the thin-walled, 4 mm. tube and the two wires of 0.23 mm. diameter, the rate of cooling after adsorption was very small. A sensitive galvanometer of five seconds period recorded a deflection of 1 mm. per 0.002° C. on a photographic sheet placed on a rotating drum 1.3 meters away. The inner tube, blown as thin as possible, to avoid a high thermal capacity, weighed 9 grams and contained 78 grams of copper. Since relative rather than absolute values were of greatest importance, the apparatus was not complicated by inserting a heating coil for calibration; but the water equivalent of the calorimeter was calculated directly from the known weights and specific heats of copper and pyrex glass.⁸ The exact portion of the inlet tube which should be included in this calculation was indeterminate; but since the total contribution of the glass to the 8.9 calories thermal capacity of the calorimeter was only 1.8 calories, this uncertainty would not exceed a

Results.

Non-uniform Adsorption of Carbon Monoxide (Initial Portions).—

The method had the distinctive feature in common with that which has been used by Garner and his co-workers⁹ for measurements on charcoal and on the methanol catalysts, that the single thermo-junction was placed in direct contact with the catalyst mass and therefore responded quickly to any changes in temperature occurring locally therein. This made it possible to obtain experimental evidence for the non-uniformity of adsorption of carbon monoxide on copper.

⁸ It will be shown later that even with a 0.5 mm. gas pressure inside the calorimeter, thermal distribution was by no means instantaneous. There is some question, therefore, whether the whole 1.8 calories water equivalent of the glass should be included, since no doubt there was some lag between the temperature of the main body of the catalyst and that of the glass.

⁹ Blench and Garner, *J.C.S.*, 125, 1288, 1924; Garner and McKie, *J.C.S.*, 2451, 1927; McKie, *J.C.S.*, 2870, 1928; Garner, *Nature*, 114, 932, 1924; Garner and Kingman, *loc. cit.*, 6.

For understanding this evidence, it will be helpful to consider the types of time-temperature curve which would result from uniform and from non-uniform adsorption. If the adsorption were uniform, the temperature would rise rapidly to a maximum value as shown in Curve (a) Fig. 2¹⁰ and then fall away slowly in a manner dependent upon the rate of loss of heat from the calorimeter across the vacuum by radiation or by conduction along the wires, glass or residual gas in the small inlet tube. Curve (a) will be designated as the normal curve and indicates uniform adsorption.

If the adsorption were non-uniform, then the time-temperature curves would vary greatly from the normal, and their form would be dependent on the position of the thermocouple relative to the locus of the adsorption and consequent liberation of heat. These variations from the normal would be the more marked, the slower the rate of thermal distribution within the catalyst mass. If the adsorption occurred only in a portion of the catalyst remote from the thermocouple, a slow rise in temperature as indicated by Curve (c) would be expected. On the other hand, if adsorption occurred only in the region close to the thermocouple, the temperature would rise to a fictitious maximum value and then fall off more rapidly than the normal curve as the heat spread throughout the remaining portions of the catalyst mass as in

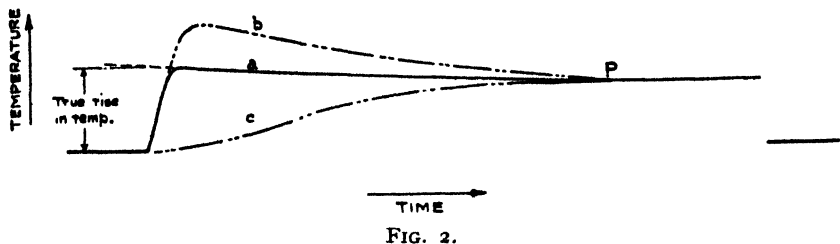


FIG. 2.

Curve (b). In either case, the Curves (b) and (c) would approximate to the normal curve at some point *P*, when the thermal distribution was complete. It is obvious that the extrapolation of Curves (b) and (c) back to zero time to obtain the true rise in temperature would be extremely uncertain, whereas in the case of Curve (a) such extrapolation could be carried out without great error.

A typical experiment showing the non-uniform adsorption of carbon monoxide will now be described. The catalyst chamber was evacuated with the thermocouple placed 1 cm. from the bottom of the catalyst mass of 7 cm. total depth. The admission of 0.2 c.c. of carbon monoxide gave rise to a time-temperature curve closely resembling the typical curve (c); about twelve minutes was required to reach the maximum temperature. When the thermocouple was moved to a point 1 cm. from the top of the catalyst, the admission of the initial 0.2 c.c. of the gas resulted in a curve of type (b). In the light of the previous discussion, these observations are adequately explained on the assumption that the adsorption of the initial 0.2 c.c. of carbon monoxide occurred on the top layer of the adsorbent. With the admission of successive increments of carbon monoxide, curves were obtained which lay all the

¹⁰ This would be true only if the rate of adsorption were very rapid. That this condition is met in the case of both carbon monoxide and hydrogen on copper can be shown by observing the pressure changes following the admission of the gas to the catalyst.

way between the extreme types (*b*) and (*c*) depending on the conditions of the experiment. A detailed discussion of these curves will not be given, but in brief it may be said that they were all consistent with the hypothesis that the adsorption of the initial increments of gas occurred on successive layers of the catalyst beginning at the top.

After about 4 c.c. of the gas had been admitted subsequent adsorptions resulted in curves which closely approximated Curve (*a*); moreover the form of the curves was independent of the position of the thermocouple. It seems evident that for the region 4 to 8 c.c. of gas admitted the adsorption occurred more or less uniformly throughout the catalyst mass. In all probability, the rate of adsorption, while still rapid, had become sufficiently slow to allow time for diffusion of the gas through the adsorbent before an appreciable amount of adsorption had taken place.

In the previous work on heats of adsorption of carbon monoxide on copper^{1,3} a small pressure (0.1 to 0.5 mm.) of inert gas was introduced to aid in the distribution of the heat. In the present research it was found that the presence of 0.5 mm. pressure of helium reduced, but by no means eliminated, the abnormalities in the time-temperature curves described above. Apparently, in cases where the adsorption does not occur uniformly, the addition of an inert gas is not sufficient to give a normal time-temperature curve.

The Uniform Adsorption of Hydrogen and of Carbon Monoxide (Later Portions).—Because the time temperature curves for the later portions of carbon monoxide adsorbed were of the normal type it was possible to read from them the values for the differential heats of adsorption over the range 4 to 8 c.c. with some assurance of accuracy. All the values for successive small quantities of the gas lay between the limits 15,600 and 13,500 calories. It should be mentioned that the residual gas pressure over this range lay between 0.5 and 3.0 mm.

For the single sample of copper studied all the time-temperature curves found when hydrogen was adsorbed were of the normal type, indicating that the adsorption process was at least approximately uniform, even for the first 0.2 c.c. adsorbed. This observation is consistent with the fact that the rate of adsorption of hydrogen at 0° C. is known to be slower than that of carbon monoxide.⁵ It is by no means established, however, that a more active sample of copper might not show the same non-uniform adsorption for hydrogen as was found in this research for carbon monoxide. In a typical series, for successive small increments of hydrogen up to 2.1 c.c. total adsorption, the differential molar heats were 13.3, 12.1, 12.3, 11.7, 13.0, 11.5 $\times 10^3$ calories. The residual hydrogen pressure changed from 0.06 mm. after the first 0.2 c.c. admitted to 3 mm. after 2.1 c.c. had been adsorbed. These normal curves for hydrogen and for the later portions of carbon monoxide all attained their maximum temperatures in ninety seconds or less.

Discussion.

It is likely that this non-uniform adsorption of carbon monoxide on copper may account for the discrepancies in the experimental data previously obtained for the initial portions. For, even in the presence of an inert gas, there would be a danger, if heat were liberated in one region only, that the whole of the calorimeter would not reach the maximum temperature actually observed. The form of the curve obtained by plotting differential heats against portion of surface covered would then

depend to a large extent on the design of the calorimeter. The author plans a further study of the problem using a calorimeter designed to eliminate as far as possible the sources of error discussed above.

There are in the literature, accounts of a large number of heats of adsorption which have been measured with thermometers or thermocouples external to the catalyst mass. In all such measurements, there would be a necessary time lag between the liberation of the heat and the observed temperature rise. This would tend to veil the abnormalities in the time-temperature curves which have been discussed above. It should be emphasised, however, that such methods would not remove the causes of these abnormalities. It seems unsafe to proceed with any measurements of heats of adsorption without first investigating the thermal changes occurring locally in the body of the catalyst. The author believes that this can best be done by use of a single junction thermocouple in direct contact with the catalyst.

Summary.

1. The heats of adsorption of carbon monoxide and hydrogen have been studied with a single junction thermocouple in direct contact with the copper catalyst.
2. Evidence is presented to show that the adsorption of the initial portions of carbon monoxide did not occur uniformly throughout the catalyst mass, but rather in successive layers.
3. For the sample of copper studied, the adsorption of hydrogen over the whole range and that of carbon monoxide for the later portions was approximately uniform and, within the limits of the experimental errors, the heats of adsorption found were independent of the amount of gas already on the surface.
4. Non-uniform adsorption is discussed as a possible source of error in all heats of adsorption measurements.
5. Further work is contemplated.

The author expresses his thanks to Professor W. E. Garner, for his advice and criticism which have been the more valuable because of his experience with heats of adsorption measurements over a period of several years; and also to Bristol University for the use of the apparatus necessary for this research.

THE SOLUBILITY OF BARIUM HYDROXIDE IN DILUTE SOLUTIONS OF SODIUM HYDROXIDE.

BY SIDNEY MAURICE NEALE AND WILLIAM ARTHUR STRINGFELLOW.
(*College of Technology, Manchester.*)

Received 2nd August, 1932.

In the course of an attempt to interpret the simultaneous absorption of sodium and barium hydroxides by cellulose, it was found that the existing data ^{1, 2, 3} for solubility of barium hydroxide in sodium hydroxide solutions do not extend to soda concentrations below 1.5 molal. Further

¹ Seidel, *Solubilities*, 2nd Edn., New York, p. 113, 1928.

² *Internat. Crit. Tables*, 1st Edn., New York, 7, p. 343, 1930.

³ Schreinemakers, *Z. physik. Chem.*, 68, 83, 1909-10.

solubility measurements, made in the hope of throwing light on the behaviour of cellulose and the mixed alkalis, are, therefore, now put forward as data covering this lower concentration range.

Recrystallised barium hydroxide (Merck's reagent) was agitated overnight in a thermostat at 25° C. with pure carbonate free caustic soda-solution, whose concentration had been determined by careful titration with standard hydrochloric acid prepared from the constant boiling acid. After settling for several hours in a thermostat at 25° ± 0.05, a portion of the clear liquid was pipetted and titrated with the standard acid. The concentration of dissolved baryta was calculated from the change in the total alkalinity. The results are given in the following table:—

Concentration of NaOH .	equivs. /litre	o	o		
Solubility of Ba(OH) ₂ .	equivs. /litre	0.548 *	0.546	0.548	0.54
Concentration of NaOH .	0.4417	0.6135	0.9177	1.230	
Solubility of Ba(OH) ₂ .	0.3052	0.2440 0.2450	0.1729 0.1725	0.1215	0.1207
Concentration of NaOH .		1.837			
Solubility of Ba(OH) ₂ .		0.083 0.086 0.082			

* Ref. 2.

THE ELECTROLYSIS OF FUSED ACETATES AND PROPIONATES.

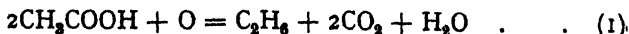
By G. B. MOORHOUSE.

Received 9th August, 1932.

Previous work on the electrolysis of fused acetates has been done by Lassar Cohn,¹ by Berle,² and by Petersen.³ These authors record widely varying results. Lassar Cohn got no anode hydrocarbon, Berle obtained methane, and Petersen obtained a varied product containing methane, ethane and ethylene. Both Lassar Cohn and Berle used potassium acetate. Petersen used mixtures of acetates, and was able to work at lower temperatures.

The chief interest of the electrolysis of fused acetates lies in its bearing on the much-worked-on problem of the electrolysis of acetate solutions, especially on the conflict between the "Oxidation" and "Discharged Ion" theories. A review of the evidence on this problem, and references to earlier work, is given by Gibson,⁴ who supports the Oxidation theory, and by Fairweather and Walker,⁵ who uphold the Discharged Ion theory.

The root question is whether the reaction



¹ Lassar Cohn, *Lieb. Ann.*, **251**, 357, 1889.

² Berle, *Ber.*, **27**, 325, 1904.

³ Petersen, *Z. Elektrochem.*, **20**, 328, 1919.

⁴ Gibson, *J.C.S.*, **127**, 475, 1925.

⁵ Fairweather and Walker, *J.C.S.*, **3111**, 1926.

actually takes place. For the production of anodic oxygen water is necessary. Hence, if a Kolbe synthesis can be got in a non-aqueous medium, or in the fused state, here at any rate the oxidation mechanism is inapplicable, and there is a presumption that it is wrong in solution also. From solutions of acetates in anhydrous acetic acid,⁶ and in methyl alcohol⁷ high ethane yields have been obtained. From fused salts, on the other hand, only in Petersen's results is there even an approximation to similarity.

A second point of issue regarding the mechanism of the general reaction has arisen through the work of Fichter,⁸ who maintains that acetyl peroxide is an intermediate. Since peroxides may be formed either by the union of discharged ion residues or by oxidation of acetic acid, this is distinct from the first issue. The products of peroxide decomposition are rather widely different from the products of electrolysis, especially in regard to methane formation. Recently O. J. Walker⁹ has shown that, under restricted conditions, namely at low current densities, some methane is, in fact, formed in electrolysis. The formation of methane by electrolysis of fused salts has been claimed by Fichter as support for the peroxide theory.

The wide variability of the fused acetate results, not only among different authors, but even between results by the same author under identical conditions, make it likely that secondary reactions are occurring. The incorporation of a hydrogen voltmeter would have afforded some check on the constancy of the anode product, but this has not hitherto been done. The purpose of the following work was to investigate the electrolysis under conditions such as to minimise secondary effects.

Fused Acetates.

Experimental.

A mixture of lithium, sodium and potassium acetates in the molar ratios of 7 : 10 : 10 was used and electrolysed at 200° C. The melt was prepared by evaporating down a solution, which passed smoothly into the melt. To drive off any water the melt was heated to 270° C. for a short time : it was then cooled to 230° C. and put under suction till bubbling ceased. Electrolysis was then begun. The cell is shown diagrammatically in Fig. 1. The anode was normally a polished platinum spiral of surface area 1 sq. cm. The cathode was a lead wire, designed to absorb the liberated alkali metals. A certain amount of cathodic hydrogen was, however, evolved during electrolysis. This points to the melt not being absolutely anhydrous. The merest trace of water is required to liberate hydrogen from sodium at 200° C. A hydrogen voltmeter was in series with the cell. The conductivity of the melt was so low that it was necessary to have as much as 30 volts across the cell to secure reasonable evolution. Before electrolysis the air in the anode tube was displaced by carbon dioxide. The evolved gas was collected over CO₂-water in a water-jacketed gas-burette, in which the confining liquid was run off as fast as the gas entered. Before removal of a sample for analysis the anode gas in the dead space was displaced into the collecting tube by a current of carbon dioxide.

⁶ Hopfgartner, *Monats.*, **32**, 523, 1911.

⁷ Salauze, *Bull. Soc. Chim.*, **37**, 522, 1925.

⁸ A review of the peroxide theory is given by Fichter in *J.S.C.I.*, **48**, 347T., 1929.

⁹ Walker, *Trans. Far. Soc.*, **27**, 35, 1931.

The evolved gas had a smell of methyl acetate. By introducing a CO_2 -snow-cooled trap between cell and collecting burette a minute condensate (about 0.02 c.c.) was obtained, and the presence of ester qualitatively shown by a positive saponification result. In a rough quantitative determination 90 per cent. of the weight of the condensate was accounted for by saponification. The weight of ester corresponded to 3 per cent. of ester vapour in the anode gas. This is obviously a minimum value. Normally, no trap was used. The ester vapour was then removed by the water in the collecting tube and by the strong potash

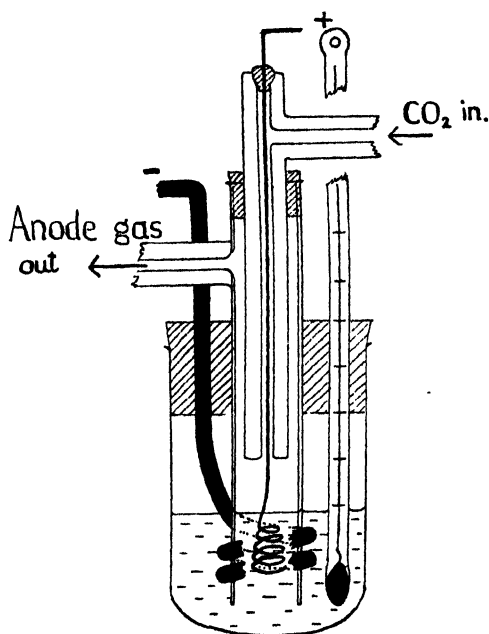


FIG. 1.

used to absorb carbon dioxide. To ensure this, the gas was left for an hour over the potash.

Gas analysis was done in a Bone-Newitt apparatus. The following gases were found:—

1. Carbon dioxide—determined by difference, the collecting burette and the gas analysis apparatus being inter-calibrated.
2. Carbon monoxide—small and variable, absorbed in ammoniacal cuprous chloride. In case the variability was due to faults in analysis, the carbon monoxide in four runs was determined by oxidation with copper oxide at 270°C .¹⁰ The results here also varied, but were similar to those obtained by the first method.
3. Trace of ethylene—absorbed by bromine in potassium bromide solution, when the volume of analysed gas was large, otherwise ignored.
4. Trace of hydrogen—absorbed by palladium black at 100°C .
5. Hydrocarbon residue—this flashed as an ethane methane mixture containing about 5 per cent. methane. Methane was positively identified by separation with liquid air. In a series of experiments the following values were got for r/c of the small condensable part: 1.8, 1.8, 1.6, 1.9, 1.8, 2.0, mean 1.8. In view of the uncertainty of flash analysis* in this range of composition the density of the dried hydrocarbon residue was regularly determined. A Kuhlmann microbalance was used to weigh the density bulb and counterpoise. In calculating the composition a small correction for gas imperfection was introduced. A linear variation of pV between $p = 1$ atmos. and $p = 0$ was assumed. Flash analyses were also corrected for gas imperfection. The density results showed, on an average, 1 per cent. less methane than the flash results. That the density results were the reliable ones was shown by experi-

¹⁰ Broom, *J.S.C.I.*, 47, 276T, 1928.

* Analysis of the hydrocarbon residue by explosion with excess oxygen.

menting with pure ethane. This gave the theoretical density (1.356), but flashed as if it contained 1 to 2 per cent. of methane. The density figures were accurate to 1 in 500, corresponding to ± 0.1 per cent. of methane in the normal anode gas.

A control experiment, in which the conditions of electrolysis were reproduced except that no current was passed, showed that no gaseous product of decomposition was formed at the working temperature. In order to see what degree of overheating would be required before decomposition began, other such controls were done at higher temperatures. Decomposition set in in the neighbourhood of 350°C . but was not vigorous. In six hours some 50 c.c. of gas were collected over potash. The composition of the gas was not constant; it consisted mainly of methane, with hydrogen and carbon monoxide also present. There was no ethane.

During electrolysis the ratio Anode gas: Voltmeter hydrogen, designated "yield" in the following, was observed continuously. Collection and analysis of successive samples showed that the constancy of this ratio was a sufficient criterion for the constancy of the anode product. There was even some latitude; variation of the yield between the limits 2.3 and 2.5 did not appear to result in appreciable change in composition.

If the yield was to be maintained it was found necessary to interrupt the current at intervals. Otherwise the yield, at first 2.5, began rapidly to decrease after a few minutes. The decrease continued until actually more hydrogen than anode gas was being evolved. Concurrently the conductivity and the temperature rose, and analysis showed that the composition of the gas was changing, methane and carbon monoxide increasing at the expense of ethane. There is little point in collecting such a sample. The interrupted method of electrolysis was therefore always used. The exact duration of the intervals did not matter. After the electrolysis had been going for some time the current always fell off, sometimes to a third of its original value. With smaller currents longer intervals could be used without the yield decaying. The amount of gas that could be obtained at constant yield was not indefinite, but by "nursing" the yield as much as 150 c.c. could be got before a decline set in.

The melt, which was clear and colourless before electrolysis, normally remained so until some 40 to 50 c.c. had been evolved. It then began to darken and rapidly became opaque. No change in the composition of the anode gas coincident with this blackening could be detected. It is evidently not a fundamental decomposition of acetate. It was found to be due, not to charring, but to partial disintegration of the lead cathode consequent on the continued absorption of the alkali metals. In experiments in which acetic acid was added to the melt there was no darkening, although 200 c.c. of gas were collected.

Results.

The results, both under normal and modified conditions, are grouped together in Table I.

No. 1 gives the normal anode product and shows the degree of reproducibility obtainable by the method of interrupted electrolysis described. For comparison the result of continuous electrolysis is given in runs 3 and 4. In No. 2 the first 15 c.c. of a large number of runs were

770 ELECTROLYSIS OF FUSED ACETATES AND PROPIONATES

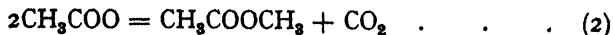
combined in order that the hydrocarbon could be accurately determined by density. The reason for the other modifications will appear later.

TABLE I.—FUSED ACETATE ELECTROLYSIS.

Ref. No.	Yield.	Percentage Composition of Anode Gas.						Volta. H ₂ in same Units.	
		C ₂ H ₄ .	H ₂ .	CO.	CH ₄ .	CO ₂ .	C ₂ H ₆ .		
Polished Platinum Anode	1 *	2.40 ± 0.05	0.2 ± 0	Normal anode product.				28.8 ± 3	41.6 ± 1.0
				0.2 ± 1	0.8 ± 2	1.3 ± 2	68.7 ± 2		
	2	2.45	—	Combined first portions.				26.1	41.0
				0.2	0.6	1.6	71.5		
	3	1.06	0.2	Continuous electrolysis.				13.0	94
				0.6	4.8	2.9	78.5		
	4	0.92	0.1					6.2	109
				1.3	6.9	2.2	83.3		
	5A †	1.7	—	Water added.				19.0	59.0
				0.0	0.6	4.2	76.2		
				0.2	0.5	2.5	72.9		
				0.0	1.2	4.6	83.8		
	5B	2.0	—					23.9	50.1
				0.0	0.6	2.6	84.3		
	6A †	0.89	—					10.4	111
				0.0	0.6	2.6	84.3		
	6B	0.95	—					12.6	106
				0.0	0.6	2.6	84.3		
7	2.39	0.2	Anhydrous acetic acid added.				28.0	41.8	
			0.3	0.8	1.6	69.1			
8	2.44	0.2					28.5	41.0	
			0.0	1.0	1.7	68.6			
9A †	0.72	0.1	Platinum black anode.				3.3	139	
			0.0	15.5	3.1	78.0			
			0.5	6.3	4.4	71.8			
			0.1	13.0	4.8	78.4			
			0.1	6.4	3.9	77.5			
9B	1.37	0.3					16.7	73	
			0.0	15.5	3.1	78.0			
10A †	0.73	0.3					3.4	137	
			0.0	15.5	3.1	78.0			
10B	0.96	0.3					11.8	104	
			0.0	15.5	3.1	78.0			
11	0.6	—	Gold anode.				1.0	137	
			21.4	0.3	77.3	1.0			
12	0.69	0.1					4.7	104	
			14.1	2.0	79.2	4.7			
13	1.92	0.2	Carbon anode.				24.4	52.1	
			0.1	2.4	3.6	69.3			
14	1.84	0.3					22.9	54.4	
			0.1	3.5	4.3	68.9			

Discussion.

The normal anode product is seen to be similar to that got from aqueous solution. For a perfect ethane synthesis we should have Ethane = Voltameter hydrogen = $\frac{1}{2}$ Carbon dioxide = 33.3 per cent. The formation of ester has already been noted. According to the equation



ester vapour is accompanied by an equal volume of carbon dioxide, and corresponds to an equivalent volume of voltameter hydrogen. It is interesting that the values of (CO₂ - 2C₂H₆) and (Volta. H₂ - C₂H₆) obtainable from No. 1 do not differ greatly. The mean values are 11.1 and 12.8 respectively. By ignoring the methane and carbon monoxide the results can therefore be explained by postulating 11 to 12 per cent. of ester formation. This, however, is well in excess of the amount of

* Mean of 13 runs. Average numerical deviation from mean added.

† Successive samples.

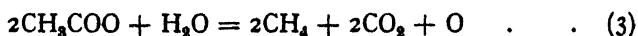
ester trapped (3 per cent.). The methane and carbon monoxide should doubtless be associated with carbon dioxide and voltameter hydrogen, but their amount is too small to do more than slightly lessen the discrepancy. It has been established that ester is formed, and in more than a trace, but the exact extent of the formation must be left open.

The amount of ethane is so considerable as to render any other mechanism of formation than the union of discharged ions out of the question.

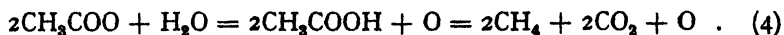
The smallness of the methane and carbon monoxide, together with the uncertainty regarding the extent of ester formation, make it impossible to test any formation mechanism from the normal anode product. In the individual results, the mean of which is recorded as No. 1 in Table I, it was noticed that, although there was no constant ratio between the amounts of these gases, they nevertheless appeared to increase or decrease together. It is thus likely that they are conditioned by some common factor. The formation of both methane and carbon monoxide by thermal decomposition of the melt at 350° C. has been referred to. It is possible, although unlikely, that such a degree of superheating occurs at the anode. Against such an origin is the production of the gases right from the beginning of the electrolysis, and the fact that they are formed in increasing amount as the yield falls. Thermal decomposition would be superimposed on the normal electrode process, and would be more likely to cause a rise in the yield. If thermal decomposition be excluded, the gases must arise from a reaction in which the discharged ions are concerned. They are both decomposition products of acetyl peroxide, and therefore to be expected on the peroxide theory. This, however, shelves the real difficulty, namely to formulate an equation for their origin, which is just as hard to do from $(\text{CH}_3\text{COO})_2$ as from $2\text{CH}_3\text{COO}$.

The theory outlined below, while finality is not claimed for it, has at least the merit of co-ordinating many of the facts about the formation of these gases. It rests on the assumption that the melt is not absolutely anhydrous.

If we admit water as a reactant, then methane may be formed, either :



or :



The continuous nature of the transition from solution to melt enabled the effect of actually adding water to be investigated. The melt was prepared as usual, and just before electrolysis about 0.5 c.c. of water was added and stirred in. On account of evaporation, the exact amount is unimportant. The results are recorded in Table I. Rather more water was added in No. 6 than in No. 5.

Comparison with the normal product shows that the methane and carbon monoxide are increased and the ethane depressed. That the ethane does decrease in the presence of water is worth emphasising. Whatever be the mechanism of methane formation, it shows that for ethane formation water is not necessary. As these runs continue, there are signs of a return to normal, reasonably explained by loss of water through evaporation. It is true that the oxygen required as a product of both these equations is absent : but at the working temperature one

would expect any anodic oxygen to be used in oxidation. The increased carbon dioxide content may be interpreted as evidence for this. Ion oxidation would give rise to water as well as carbon dioxide. It therefore requires the original presence of only a trace of water for methane to be continually formed. Thus, although on this theory an absolutely anhydrous melt should give no methane, such a melt would be difficult to secure.

Carbon monoxide is best explained as a product of partial oxidation. This would provide for a general connection between methane and carbon monoxide such as has been observed. Oxidation to give either carbon monoxide or dioxide gives a small volume of anode gas per unit voltameter hydrogen; total oxidation, for example, gives anode gas = $\frac{1}{2}$ voltameter hydrogen. The lowering of yield which sets in with continuous electrolysis is therefore to be connected with the increased carbon monoxide content under these conditions, and the effect of interruption in maintaining a constant product interpreted as the affording of an opportunity for the water vapour formed by the oxidation to escape from the anode surface.

As between the two suggested equations for methane formation, (4) certainly appears more probable. An attempt to distinguish between the two possibilities was made by electrolysis after the addition of a small amount of anhydrous acetic acid to the melt. An increased methane content under these conditions would be definitely in favour of (4). The result is recorded in Table I. It will be seen that only a very small increase was observed: on the other hand, the tendency of the yield to decay, which accompanies methane formation, was less pronounced than in normal electrolysis. While, on the whole, this appears to favour mechanism (3), mechanism (4) is still possible if it is only the acetic acid "nascent" at the anode surface which is in a condition to split up.

The effect of varying the anode material is recorded in the lower part of Table I. The metal anodes were of the same surface area as the polished platinum one. The carbon anode—a high-grade arc carbon—had a surface area of 3 sq. cm. A constant and fairly reproducible product was obtained with carbon, but not with either of the other anodes.

The well-known specificity of the anode in aqueous solution is usually associated with the extent to which the action of water on the discharged ions is accelerated. The degree of specificity found in the fused state is surprising, and difficult to explain other than by the assumption of an imperfectly anhydrous melt. With gold and platinum black the product, in particular the high carbon monoxide and dioxide content, is similar to that obtained by continuous electrolysis. On the hypothesis outlined above, this indicates that these anodes are more sensitive to the presence of water than is polished platinum.

Electrolysis with a gold anode was unsatisfactory, as the melt rapidly went black in the neighbourhood of the anode. With platinum black the synthesis became better as the electrolysis proceeded. This was possibly due to a deposit of carbon. The very fair synthesis with carbon is interesting, especially as this anode is without oxidising properties. It may be compared with the synthesis of ethane at graphite anodes in aqueous solution recently announced by Fichter.⁸

Fused Propionates.

The methods developed for acetate electrolysis were applied to propionate electrolysis. There has been very little previous work on this subject. Berle observed that potassium propionate was too unstable to electrolyse. Petersen³ electrolysed lead propionate at the low temperature of 130° C. The gas he obtained was variable, contained no butane and in general bore little resemblance to that got from aqueous solutions or from solutions in propionic acid. He electrolysed continuously, and in the light of the results here recorded it is probable that thermal decomposition was occurring.

The melting-points of the alkali propionates are higher than those of acetates. Tests with mixtures of lithium, sodium and potassium propionates showed that the binary 1 : 1 molar lithium sodium mixture had the lowest melting-point. The lowest convenient working temperature was 230° C. The conductivity of the melt was even lower than that of acetate; 35 volts were required before the gas was evolved at a reasonable rate. The same electrodes were employed which had already been used for acetate electrolysis.

The anode product contained carbon dioxide, unsaturated hydrocarbon (recorded as ethylene), a small amount of carbon monoxide, an occasional trace of hydrogen and a hydrocarbon residue which was not pure butane. Separation of the residue with liquid air showed that methane was absent. Further fractionation with frozen petrol ether and with CO₂-snow showed that propane, if present, was not greater than 5 per cent. of the residue. Propane is *a priori* unlikely. It was therefore concluded that the saturated hydrocarbons were butane and ethane.

In six runs, where the amount of gas available was sufficient, the results of flash analysis were checked by density measurements. Any requisite corrections for gas imperfections were applied both in flash and density analysis. The ethane percentage in the hydrocarbon deduced from density was regularly less than that deduced from flashing by about 2 per cent., corresponding to a difference of 0.6 per cent. in the anode gas. In cases where the amount was insufficient for a density determination a correction of this amount was made in the recorded ethane and butane percentages, on the assumption that here, as in the ethane methane mixture, the density figures are the reliable ones.

The smell of ethyl propionate was noticeable during a run. By experiments analogous to those described for acetates the presence of ester was qualitatively proved. Quantitatively, variable results were obtained, always less, however, than for methyl acetate. Owing to added difficulties of trapping ethyl propionate the significance of this is doubtful.

Control experiments showed that, at the working temperature, no gas was evolved by thermal decomposition. By raising the temperature to about 350° C. thermal decomposition set in, yielding a gas which, after collection over potash, consisted mainly of ethylene and carbon monoxide, with hydrogen, methane and ethane in smaller amounts.

The results of electrolysis are grouped together in Table II, and in the main have their parallels in the acetate runs of Table I. Although the same interrupted technique was employed as for acetates there was not the same control over the yield. A slow downward drift set in after some 15 c.c. had been collected. This was reflected in a change in the anode gas, more particularly in an increase of ethane at the expense of

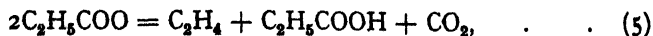
TABLE II.—FUSED PROPIONATE ELECTROLYSIS.

Ref. No.	Yield.	Percentage Composition of Anode Gas.						Volta. H ₂ in same Units.	
		H ₂ .	CO.	C ₂ H ₄ .	C ₂ H ₆ .	CO ₂ .	C ₄ H ₁₀ .		
Normal conditions—varied yields.									
Polished platinum anode.	1	2.23	0.3	0.2	4.0	13.9	65.4	44.8	
	2	2.16	0.5	0.6	4.8	13.6	64.8	46.3	
	3	2.06	0.8	1.4	6.4	9.4	67.1	48.5	
	4	1.94	0.5	1.6	7.2	12.1	64.9	51.6	
	5	1.74	1.1	3.5	15.4	8.9	63.1	57.5	
	6	1.58	1.3	3.6	16.8	7.4	65.1	63.5	
	Normal conditions—first portions.								
	7 *	2.40 ± .05	0.1 ± 0	0.4 ± .1	7.3 ± 1.1	8.7 ± 1.0	65.0 ± .3	18.5 ± .5	41.6 ± 1.1
	Anhydrous propionic acid added								
	8	2.56	0.4	0.2	6.1	8.3	64.5	20.5	39.2
9	2.49	0.2	0.2	5.5	8.8	65.0	20.3	40.1	
Platinum black anode.									
10A †	2.15	0.5	0.5	11.5	6.7	64.3	16.5	46.5	
10B	1.72	0.0	1.2	7.9	12.6	65.2	13.1	58.0	
11A †	2.06	0.4	0.5	9.4	6.1	66.7	16.9	48.7	
11B	1.76	0.4	2.0	8.6	10.7	65.0	13.3	57.0	
Gold anode.									
12A †	1.46	0.0	0.4	6.7	14.4	69.3	9.2	68.5	
12B	1.73	0.1	1.3	6.9	16.6	63.2	11.9	58.0	
13A †	1.45	0.0	0.4	6.2	15.5	68.9	9.0	69.0	
13B	1.71	1.2	1.6	8.4	14.4	63.3	11.1	58.6	
Carbon anode.									
14	1.92	0.0	1.2	5.9	12.2	66.7	14.0	52.3	

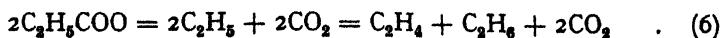
butane (see No. 1-6). The first 15 c.c. of gas in four runs were analysed separately; they gave fairly reproducible results. The mean is recorded as No. 7. This is probably the best analogue of the "normal anode product" of acetate electrolysis. In this connection it is interesting that the addition of propionic acid (No. 8 and 9) enabled the initial product to be maintained while over 100 c.c. were collected.

The only feasible mechanism for butane formation is the obvious one, namely union of discharged ions.

The ethylene formation has no parallel in acetate electrolysis. It may be formed in the same way as ethylene from aqueous solution. This reaction is usually formulated:—



although there is no definite evidence in its favour, and it seems *a priori* unlikely. Alternatively it might arise by the reaction:—



which links ethylene with ethane. This looks a more likely reaction. All the ethylene, however, cannot arise in this way, as ethane is normally less than ethylene.

* Mean of four runs. Average numerical deviation from mean added.

† Successive samples.

The ethane may be compared with the methane from acetate, and the same correspondence between the yield and the amount of lower hydrocarbon noted. A mechanism involving the presence of water has been suggested for methane. The cathodic evolution noted for acetate also occurred with propionate. Unlike acetate, however, the propionate has little affinity for water. It does not pass smoothly from solution to melt, and rejects water violently when a drop is added, so that the effect of adding water could not be investigated. The poor synthesis at gold and platinum black anodes was interpreted as evidence for the presence of water: but with propionates a very fair synthesis is got with these anodes, even at the beginning of the electrolysis. But although there is less evidence for the presence of water there is more ethane. It would therefore seem probable that at any rate the major part of the ethane comes from a different mechanism.

It is possible, however, to account for ethane without postulating the presence of water, by a mechanism which is nevertheless essentially the same as that for methane formation, namely the decomposition of "nascent" acid. In the case of acetate this can only come from the action of water on the ions; but with propionate nascent propionic may be formed in the course of ethylene formation according to equation (5). This also accounts for the much larger ethane than methane formation. That the acid requires to be nascent is shown by runs 8 and 9 of Table II, in which propionic acid was added to the melt; the ethane percentage was not increased. In so far as it links ethane with ethylene this mechanism is similar to that of equation (6). The link, however, is not so rigid, in that all the acid need not decompose. The only condition imposed is that ethane should not be greater than ethylene, which is in the main in agreement with the results.

Bearing of the Results on the Peroxide Theory.

All the equations suggested for the various anode products may be formally expressed in terms of the peroxide theory by introducing the step $2RCOO = (RCOO)_2$. Both peroxides are explosive at temperatures below those used in electrolysis, so it is idle to attempt to isolate them. The anode gases may be compared with the product from the thermal decomposition of peroxides.¹¹ The gas from acetyl peroxide is qualitatively similar to that got by electrolysis of acetates; the proportions, however, differ considerably. Decomposition of the peroxide by ultra-violet light¹² yields a product more closely resembling that from electrolysis. With propionates the discrepancies are wider. Instead of the ethane butane mixture obtained from the fused salts a 60 — 40 methane butane mixture was obtained from the thermal decomposition of propionyl peroxide. Ethane, even in quantity, might have escaped detection with the method of analysis used by Fichter and Krummenacher. Methane is definitely absent in electrolysis.

From the point of view of the peroxide theory this correspondence cannot be regarded as satisfactory. In the absence of positive evidence it hardly seems worth while postulating a second highly unstable product at the anode surface when one such product, the discharged ions, is already present.

¹¹ Fichter and Krummenacher, *Helv. Chim. Acta*, **1**, 147, 1918.

¹² Walker, *J.C.S.*, 2040, 1928.

Summary.

1. In the electrolysis of fused acetates and propionates the main products are those of the corresponding Kolbe reaction in aqueous solution.
2. The variable results of previous workers are attributed to the occurrence of secondary decompositions. Conditions of electrolysis are described by which these effects are minimised. With acetate a uniform product can be obtained. The propionate results are less reproducible.
3. The most probable mechanism for these syntheses is the interaction of discharged ions.
4. The transitory formation of peroxides by the interaction of discharged ions is not excluded, but there is little positive evidence in its favour.
5. As by-products of the electrolysis are formed :—
 - (1) Methane from acetate and ethane from propionate. A tentative mechanism for this reaction, namely decomposition of nascent acetic or propionic acid, is proposed and evidence is given in support.
 - (2) Carbon monoxide from acetate and in lesser amount from propionate. It is suggested that this arises from partial oxidation of discharged ions.
 - (3) A certain amount of ester.
6. The effect of varying the anode material has been studied. Specificity is more marked for acetate than for propionate. With acetate very little Kolbe synthesis is got at platinum black or gold anodes, although both give a moderate synthesis with propionate. A carbon anode gives a synthesis with both acetate and propionate.

The author has pleasure in acknowledging his indebtedness to Prof. Sir James Walker for his encouragement and advice throughout the work. His thanks are also due to the Earl of Moray Endowment for a grant towards the purchase of a Bone-Newitt gas analysis apparatus.

*Chemistry Dept.,
University of Edinburgh.*

REVIEWS OF BOOKS.

Molecular Rays. By RONALD G. J. FRASER. Pp. vii + 204. (Cambridge : University Press. 1931. Price 12s. 6d.)

The technique of molecular rays has been so highly developed within recent years and such striking results have been achieved that we are fortunate to have a volume, devoted exclusively to the subject, from one who has received his training in the great Institute at Hamburg and has made important contributions to the subject himself.

The first chapter is devoted to an account of the production and measurement of molecular rays. There is a full and frank discussion of the various detectors which have so far been used and an assessment of their merits and demerits. The gaps in the technique are pointed out and a stimulus is thus given to further experimental research in this field.

Later chapters deal with the scattering, reflection and diffraction of atoms and molecules from solid surfaces. Little is known theoretically as to the conditions under which a molecule is instantaneously reflected or adsorbed and then re-evaporated, so that it is valuable to have collected together such experimental

evidence as exists as to the time of adsorption of impinging atoms on surfaces, and the conditions for specular reflection. The great progress which has been made in detecting the diffraction of atoms from surfaces is fully reviewed, and it is shown how strikingly such experiments have confirmed the wave nature of molecular beams.

The famous application of the molecular ray technique to deduce magnetic moments of atoms by Stein and Gerlach is described at great length, as it should be and an expert summary is given of the achievements and limitations of the method. An account is also given of the progress which has been made in applying similar analogous methods to the determination of the electric moments of molecules, though there is room for considerable development in this direction.

The book is excellently written in a clear and simple style. Mathematical formulæ are reduced to a minimum so that none should be deterred from reading it. It can confidently be recommended to undergraduate as well as to post-graduate students of physics and chemistry.

II Polarografo, sua teoria e applicazioni. (The Polarograph, its theory and applications.) By GIOVANNI SEMERANO. (Padova, Libreria Editrice A. Draghi di G. Randi Fu C. B., 1932, X. 8, pp. iv and 207, with 31 Figs. Price, Lire 16.)

The numerous communications dealing with the special electro-analytical method with the dropping mercury kathode have now been collected together in a monograph by Dr. G. Semerano, lecturer of physical chemistry at the University of Padova. In the researches described the capillary electrode, originally used by B. Kucera for electro-capillary measurements analogous to the Lippmann electrometer method, is applied. J. Heyrovský was the first to measure the current passing through the dropping mercury kathode, and showed that this current furnishes an excellent means for qualitative as well as quantitative analysis. In order to render this type of analysis automatic, J. Heyrovský, in collaboration with M. Shikata of the Kyoto University, has invented a machine, "Polarograph," which registers photographically the current-voltage curves, from the shape of which analytical deductions are drawn. Hence the name "polarographic analysis".

The rapid growth of this special line of investigations is seen, when we compare G. Semerano's independent publication, covering over 200 pages, with the brief reports hitherto given, e.g. S. Prát's, in Abderhalden's *Handbuch* (1928), St. Swietoslowski's *Elektrochemia* (1930) and W. Kemula's in *Z. Elektrochemie*, **37**, 779 (1931).

The author commences with the fundamental electro-chemical and physical principles of the polarographic method, contributing here himself an original mathematical analysis of current-voltage curves. Then the results hitherto obtained in pure and applied inorganic and organic chemistry are described; the new achievements in electro-chemistry are perhaps most conspicuous when considering the treatment of problems of over-voltage, the mechanism of splitting of complex ions, and new phenomena of electro-adsorption. Further, examples are described bearing on physiological, pharmaceutical and medical chemistry. The monograph concludes with cases of practical analysis, which have hitherto been found advantageous in applied chemistry, viz. in the examination of the products of fermentation and in the sugar and petroleum industries.

The monograph contains well reproduced polarograms, and a good photograph of the late type of "Polarograph" as manufactured in Prague by Dr. V. and J. Nejedlý.

The book includes a complete "Bibliografia Polarografica," recording 105 different papers, thus giving full information and advice so as to instruct a beginner in the technique of polarography. It may be warmly recommended to all interested in the evolution of electro-chemistry and physical methods of chemical analysis.

J. H.

Nachträge zum Atlas der physikalischen und anorganischen Chemie. Von A. VON ANTROPOFF UND M. VON STACKELBERG. (Verlag Chemie G.m.b.H., Berlin, 1932. Pp. 10. Price 3 marks.)

This supplement to the Atlas contains new complete tables for ionic radii, ionisation potentials, crystal structure, melting- and boiling-points of the elements, and heats of combustion and affinities. In other cases the number of new determinations is so small that the isolated values only are given instead of repeating the whole tables. The ionisation potentials are all those found spectroscopically which differ so much from the old values that a new graph is also provided. All who possess the Atlas should obtain this supplement, which will fit into the case holding the sheets. Since some of the tables are complete, the supplement will also be found useful to those who do not require the complete Atlas.

J. R. P.

Die technische Elektrolyse Wässriger Lösungen. (Handbuch der Technischen Elektrochemie.) Vol. 1. Part 2. VICTOR ENGELHARDT. (Leipzig: Akademische Verlagsgesellschaft M.B.H., 1932. Price 30 m. Bound 32 m.)

The present volume is devoted to the electro-metallurgy of aqueous solutions of gold, silver, and copper compounds, and includes a short section of six pages on the electrolytic recovery of a number of rare metals of least industrial importance such as gallium and indium. As was apparent in the earlier volume, Part 1, this work comprises a thorough survey of modern technical practice and methods in the leading refineries, the majority of which are situated in America.

The sections on the refining of gold, silver, and copper, using soluble anodes, are contributed by W. Schopper, and that on the electrolytic extraction of copper with insoluble anodes by G. Eger, while a chapter on the rare metals is written by M. Hosenfeld. The authorship of these monographs thus ensures the material being compiled from an intimate practical knowledge of the technical details of the processes described. The value of the work to the chemical engineer is enhanced by the numerous illustrations, flow sheets, and sketch diagrams of plant lay-out.

The main general impression given by a study of this volume, as with the section on other metals dealt with in the earlier volume, is the extent to which electrolytic methods have progressed in one direction for obtaining metals of a higher degree of purity, and thus meeting the requirements of modern metallurgical practice which become continually more exacting, and in another direction for the more efficient extraction of metals from the raw materials. In many instances the material treated consists of complex or low-grade ores which cannot be smelted economically by pyro-metallurgical operations, or which have been rejected as by-products from such processes.

The importance of a high degree of purity with copper is shown by a detailed tabulation of data on the conductivity of the metal when containing varying small amounts of other metals. In this section on copper, data on comparative

working conditions at the largest copper refineries are tabulated in a useful form, and the plant of the Ontario Refining Company in Canada is described in detail. An item of interest is the information that of the total annual world production of 1,760,000 tons of refined copper, 86.5 per cent. is now electrolytic, while, of this, about 9 per cent. is derived by direct electrolytic extraction from the ore. With zinc, in comparison, the proportion of electrolytically extracted metal to the total world output amounts to 28 per cent.

In the electrolytic extraction of metals, noteworthy developments in the preparation of insoluble anodes are brought to notice.

An interesting outcome of researches on polarisation phenomena is seen in the adoption of superposed alternating current in the Wohlwill process for the refining of gold.

J. N. P.

Vision and Colour Vision. By R. A. HOUSTOUN, M.A. (Longmans, Green & Co., London. Pp. 238. $21\frac{1}{2} \times 13\frac{1}{2}$ cms. Diagrams. 15s. net.)

Dr. Houstoun's previous publications on the subject of vision and colour vision prepare one for an exposition displaying considerable independent thought. The subject is still in the land of doubt; and much very good-tempered debate has even recently (Phys. Soc.) taken place upon it. Until the publication of that discussion we do not know what influence the author's exposition of his views may have had. The energy in a light beam can of course be measured by some such instrument as a thermopile. This, however, does not give a measure of the sensation which the beam can excite and it has been disputed as to whether such a measure of a reliable kind can be obtained.

It is one of the functions of this book to develop such a measure, and this the author proceeds to do, starting with very simple experiments, the underlying logic of which can hardly be disputed.

The book, however, is not confined to this very fundamental question. Much work has been conducted in recent times and the author gives here a very lucid and succinct account of much which has not yet found its way into textbooks.

Everyone interested in the subject ought to become a possessor of this manual.

The Calculation of Heat Transmission. By MARGARET FISHENDEN, D.Sc., F.Inst.P., and OWEN A. SAUNDERS, M.A., M.Sc. (His Majesty's Stationery Office, 1932. Pp. xii + 280. $24\frac{1}{2} \times 14\frac{1}{2}$ cm. Price 10s. net.)

The object of this book is to give references to the large amount of experimental work that has been done on this subject and to show how the results of this work can be utilised to calculate the heat transmission in cases which occur in technical practice. It differs, therefore, from an ordinary textbook in which the details of the experimental work would receive more attention. In most cases merely the results which have been obtained are quoted and the reader must turn up the original sources to find out the details on which his own powers of judgment might be exercised.

The phrase, "it can be shown" very frequently occurs; it must be understood therefore that the book is not self-dependent. This makes it a difficult book to read through in a continuous way, but may not detract from its utility as a book of reference.

The chief interest is in the diagrams, which are drawn so as to depict the heat transmission from step to step. These are co-ordinate diagrams; the authors have in no case given examples of the use of alignment charts for the problems.

solved. Important use has been made of the "method of dimensions" in the selection of the best variables to use. This is introduced notably in the case of the free and forced convection of heat in fluids. Some help from a general method of this kind was certainly necessary in trying to harmonise the varied results obtained by multifarious workers on the subject. It is obvious that different experimenters have not paid much attention to the possible influence of variables other than the few chief data controlling an experiment, or else have worked too carelessly for their data to have much value. It is high time that doubt should be removed from the data for the flow of heat in tubes. Are not the investigations of Greenwood, Acland, and Nobbs, for gases at high pressure, available or have they been buried for good in the Archives of the Ministry of Munitions?

Instruction on actual calculations begins in Chapter X. (p. 194). This is accompanied by numerous diagrams to aid calculation. The examples given will be of considerable help to a worker if he is prepared to think for himself; but a casual examination leaves one with the impression that too much has been left to the reader to do.

The subject is full of pitfalls. For example, for the pipe data to apply the pipes must be clean. In factory practice they gather anything but a silver lining and the coefficient of transmission is greatly reduced. I am not aware that this has been called attention to in this volume, but I may have overlooked it. In any case it is not given the required prominence.

In Appendix A is given a very satisfactory outline of the principle of similarity. Appendix B contains proofs of formulæ for parallel and counter flow, while Appendix C contains tables of various properties of air, CO_2 , and water.

The book is well printed as a rule, though sometimes the alignment is misleading; for example $E\lambda$ instead of E_λ (p. 15). On p. 67 the formula $4\gamma/9\gamma - 5$ is liable to misinterpretation; in the footnote, p. 79, there is bad alignment. It is a pity to use the symbol H in two senses on p. 59. E_1 is omitted from the last formula on p. 26. Throughout the volume Kirchhoff is spelt with one h .

THE FREE ENERGY OF TRANSITION OF IRON ($\alpha \rightleftharpoons \gamma$).

BY YAP, CHU-PHAY.*

Received 8th August, 1932.

The allotropic transitions of iron have been the subject of a vast amount of investigations, and to-day we have generally accepted the existence of only two forms, namely, α Fe, stable from room temperature (and presumably from absolute zero) to 900° C., when it transforms to the γ form, which is stable only up to 1400° C. The δ form, which is stable from 1400° C. up to the melting-point, is identical with the α Fe. In order to avoid misunderstanding, the transition at 900° C. is designated as the A_3 point, and the other transition at 1400° C. is the A_4 point.

In so far as the writer is aware, iron appears to be the only metallic substance which shows the curious phenomena of reversible polymorphism, because the properties of α Fe, which have been so abruptly interrupted at 900° C., are resumed at 1400° C., e.g., magnetic susceptibility, specific heat, crystal structure, density, and even carbon solubility. In other words, were it not for the presence of the γ form, iron would then show no transition at all. It has, therefore, been suggested by several physical metallurgists¹ that *absolutely pure* iron may not possess any allotropy. Later in this paper we shall discuss this point in more detail.

Until the advent of X-ray crystal analysis, it was believed that the paramagnetic β form exists from the Curie point (A_1 at 790° C.) up to the A_3 point, but since it has been shown that β Fe is also body-centred cubic structure identical with ferromagnetic iron, no true allotropic transition occurs at the Curie point as had been assumed.

In this paper, the treatment of the free energy of transition will be strictly empirical, formal, and, whenever possible, graphical. No attempt will be made to discuss the origin of ferromagnetism and its effects on the thermal properties of iron. We shall, in fact, make only one assumption throughout this paper: that the specific heat values derived by the writer from published sources are substantially correct. Reasons for this conviction will be shown below.

The Specific Heat of Iron.

Recently Umino² has again determined the specific heat of iron from 680° to 1560° C., although unfortunately he did not extend his study to room temperature. After reviewing the literature on the subject, e.g., Umino's earlier investigations,³ the work of Wust and co-workers⁴ and a

* Physical Metallurgist-Chemist, New York City, U.S.A.

¹ Consult, for example, a paper by Yensen: *Trans. A.I.M.M.E., Iron and Steel Div.*, p. 90, 1929.

² *Sci. Repts.*, Tohoku Imp. Univ., 18, 91, 1929.

³ *Ibid.*, 15, 331, 597, 1926; 16, 1009, 1927.

⁴ *Z. Instrumentenk.*, 39, 294, 1919.

782 THE FREE ENERGY OF TRANSITION OF IRON ($\alpha \rightleftharpoons \gamma$)

TABLE I.—THE TOTAL HEAT CONTENT (H) AND HEAT CAPACITY OF IRON FROM 0° TO 1600° C.

°C.	H .	Sp. Ht.	Ht. Cap.	Critical Points.
0	0.0	0.104	5.81	
100	10.8	0.112 _s	6.28	
200	22.5	0.122 _s	6.84	
300	34.7	0.134	7.48	
400	48.7	0.149	8.32	
500	64.0	0.165	9.21	
600	81.1	0.184	10.28	
700	100.1	0.204	11.39	
790	119.2	0.226 _s	12.65	A ₂
	—	0.185	10.33	
800	121.0	0.185	10.33	
900	139.5	0.185	10.33	A ₃
	145.1	0.158 _s	8.85	
1000	161.2	0.163	9.10	
1100	177.7	0.167 _s	9.35	
1200	194.7	0.172	9.61	
1300	212.1	0.176	9.83	
1400	230.1 ₄	0.181	10.10	A ₄
	231.9	0.185	10.33	
1500	250.4	0.185	10.33	
1530	260.0	0.185	10.33	M.P.
	321.6	0.194	10.83	
1600	335.2	0.194	10.83	

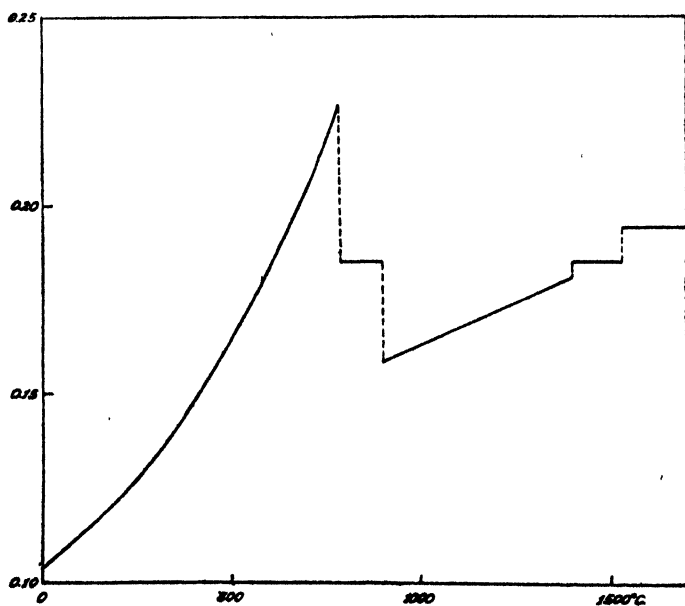


FIG. 1.—The specific heat curve of iron in cal. /g.

recent investigation by Oberhoffer and Grosse,⁵ to name but three, the writer decided it is safest to use Umino's earlier work with certain proper

⁵ *Stahl u. Eisen*, 47, 576, 1927.

correction to make it consistent with his later results. In calorimetric work on heat capacity, there is, of course, not only a constant error to be taken care of, but also a systematic error which is a function of the temperature; hence, it is not reasonable to resort to averaging the results of various workers. From the standpoint of internal evidence, the writer believes that Umino's investigations are the most reliable ones.

In Table I. is shown the total heat content (H) from 0° to 1600° C., the total heat content above 700° C. being Umino's latest values. The specific heats were obtained with the aid of a mirror tangentimeter as suggested by Latshaw,⁶ and the heat content then again obtained by means of a planimeter. The very sharp drop in the specific heat at the Curie point (see Fig. 1) is probably the reason why it appears as if a heat evolution or absorption takes place upon passing through the Curie point. It should be noted that actually due to a lag in the transformation, the change from the paramagnetic α Fe to the ferromagnetic form takes place over a range of temperature. Since the "heat of demagnetisation" is about 3.65 cal./g., according to Umino,⁸ the actual specific heat curve can be easily adjusted so that the demagnetisation takes place at 790° C., as has been done in Fig. 1. It is remarkable that the specific heat of δ Fe is identical with that of paramagnetic α Fe below 900° C. We have good reasons to assume from a study of the specific heat of other paramagnetic substances, that the specific heat of γ Fe at temperatures lower than 900° C. is merely a continuous linear function, and can be represented approximately by the equation,

$$\gamma\text{Fe}; \text{Sp. ht.} = 0.1069 + 4.403 \times 10^{-5} T \text{ cal./g.}$$

Calculations on the Free Energy of Transition.

Accepting the β form to be identical with the paramagnetic form below 900° C., we know then that the entropy of the γ form is larger than that of the α form, because, upon undergoing the transition, 5.6 cal./g. of heat are absorbed. On the other hand, at 1400° C., the entropy of the $\delta(=\alpha)$ form is larger than that of the γ form, because the heat of

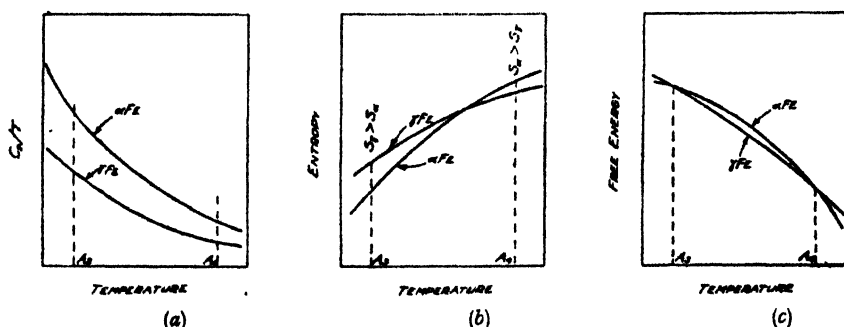


FIG. 2.

transition, $\gamma \rightarrow \delta$, is 1.86 cal./g. according to Umino.⁸ The entropy curves of both the $\alpha(=\delta)$ and the γ forms are shown qualitatively in Fig. 2 (b), from which it will be evident why the two entropy curves must intersect at some temperature between A_3 and A_4 .⁷ Since

⁶ *J. Am. Chem. Soc.*, **47**, 793, 1925.

⁷ This subject has been treated in some detail by Tammann: *States of Aggregation*. Translated by Mehl. D. Van Nostrand Co., New York. (1925).

($\partial S/\partial T$)_P = $-C_P/T$, we should expect the specific heat of γ Fe to be smaller than that of α Fe throughout the temperature range between A_3 and A_4 , and so in Fig. 2 (a) is shown the C_P/T curves of α and γ Fe. Moreover, since (dF/dT) = $-S_P$ or simply S , because as we are dealing with the change in free energy, it is understood that all values are obtained at constant pressure. In Fig. 2 (c) is shown the free energy curves of α and γ Fe, such that at 900° C. and 1400° C., $F_{\gamma\text{Fe}} - F_{\alpha\text{Fe}} = 0$, and as the free energy of γ Fe is less than that of α Fe between those two temperatures, the former is, therefore, the stable form.

From the simple Kirchhoff's law, it can be easily shown finally that the specific heats obtained by Umino must be quantitatively correct.

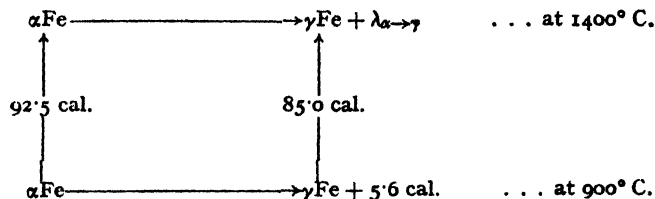


FIG. 3.

In Fig. 3 we have a cycle in which upon heating α Fe from 900° to 1400° C., 92.5 cal./g. (i.e. 0.185×500) of heat are absorbed. On the other hand, when we change α to the γ form, 5.6 cal./g. of heat are absorbed, and heating the γ Fe from 900° to 1400° C. requires 85.0 cal./g. of heat in addition (see Table II.). A simple calculation shows that the heat of transition, $\lambda_{\alpha \rightarrow \gamma}$, is equal to -1.9 cal./g., that is, at 1400° C. the $\alpha \rightarrow \gamma$ transition is accompanied by an evolution of heat. The heat of transition $\delta(=\alpha) \rightarrow \gamma$, according to Umino,² is equal to -1.86 cal./g.; hence, we conclude that no heat of transition is involved in the change from the α

TABLE II.—THE CALCULATED HEAT OF TRANSITION AT VARIOUS TEMPERATURES.

° C.	$H_{\alpha\text{Fe}}$	$H_{\gamma\text{Fe}}$	$\Delta H_{\alpha \rightarrow \gamma}$
25	2.6 ₇	3.0	20.5 ₃
200	22.5	24.7	22.4
400	48.7	51.1	22.6
600	81.1	79.3	18.4
800	121.0	109.3	8.5
900	139.5	124.9	5.6
1000	158.0	141.0	3.2
1100	176.5	157.5	1.2
1200	195.0	174.5	- 0.3 *
1300	213.5	191.8	- 1.5
1400	232.0	209.9	- 1.9

to the δ form, and the two forms are *per se* identical. The demonstration of this closed cycle shows also that the specific heat values obtained by Umino must be correct, as there is general agreement regarding the heats of transition.

Although between 900° and 1400° C. the specific heat curves of the α and γ forms are regular and therefore a simple free energy equation could be set up to determine the free energy of transition in that range

* The (—) sign indicates that the heat of transition is exothermic.

of temperature; nevertheless, it is not practicable to calculate it analytically on account of the large temperatures involved. We shall, therefore, resort to another method which is more accurate. From Table I. the total heat contents above 0° C. of α and γ Fe are obtained, as shown in Table II. The variation in the heat of transition, $\alpha \rightarrow \gamma$, can then be calculated by Kirchhoff's law, and so if we can obtain the corresponding values of ΔS , the values of ΔF can be calculated, as $\Delta F = \Delta H - T\Delta S$. Another general method is to plot $\Delta H/T^2$ against T , as

$$d(\Delta F/T) = -(\Delta H/T^2)dT,$$

and $\Delta F = 0$ at 900° C., and also at 1400° C. It is, however, not so well adapted to the present case, because the heat contents are given only to the first decimal point, whereas the specific heat values are given to 3 or 4 decimal points and so the area under the C_P/T curves can be measured far more accurately. Moreover, any error in the value of ΔH is thus automatically counter-balanced by ΔS .

Bearing in mind that $(\partial S/\partial T)_P = -C_P/T$, if we plot C_P/T against T and take the area under the curve, we thus obtain the relative entropy between any two temperatures, say 25° C. and a higher temperature. The C_P/T curves for α and γ Fe are shown in Fig. 4, from which we can obtain the relative entropy between 25° C. and any other temperature. To the relative entropy of α Fe between 25° C. and some higher temperature, we add the absolute entropy of iron from 0° to 25° C., which is 6.87 cal./g. atom or 0.12303 cal./g. according to Rodebush and Michalek,⁶ so that the relative entropy is converted to absolute entropy. From Fig. 4 the relative entropy of α Fe from 25° to 900° C. is 0.20446 cal./g.; hence, its absolute entropy at 900° C. is 0.32749 cal./g. On the other hand, the absolute entropy of γ Fe at 900° C. is larger than the absolute entropy of α Fe at the same temperature by 0.00477 cal./g. as the heat of transition, $\alpha \rightarrow \gamma$, is 5.6 cal./g.; hence, $S_{\gamma-1178} - S_{\alpha-1178} = 0.00477$ cal./g. The relative entropy of γ Fe from 25° to 900° C. is 0.18974 cal./g., so that its absolute entropy at 298° K. (25° C.) is 0.14252 cal./g. The entropy of transition, $\alpha \rightarrow \gamma$, at various temperatures is shown in Table III. It is noteworthy that the absolute entropy of γ Fe is less than the absolute

TABLE III.—THE ABSOLUTE ENTROPY OF α AND γ Fe AT VARIOUS TEMPERATURES, TOGETHER WITH THEIR RESPECTIVE ENTROPY AND FREE ENERGY CHANGE OF TRANSITION (ΔF) PER GRAM-ATOM.

° C.	$S_{\alpha\text{Fe}}$	$S_{\gamma\text{Fe}}$	$\Delta S_{\alpha \rightarrow \gamma}$	ΔF cal./ g. Atom.
25	0.12303	0.14252	0.01949	822
200	0.18221	0.20709	0.02488	594
400	0.22888	0.25308	0.02420	352
600	0.27159	0.28844	0.01685	206
800	0.31179	0.31859	0.00680	67
900	0.32749	0.33226	0.00477	0
1000	0.34262	0.34540	0.00278	- 19 *
1100	0.35661	0.35783	0.00122	- 27
1200	0.36961	0.36971	0.00010	- 25
1300	0.38176	0.38109	- 0.00067	- 25
1400	0.39316	0.39203	- 0.00113	0

⁶ J. Amer. Chem. Soc., 47, 2117, 1925.

* The (-) sign indicates that γ Fe iron is stable with respect to α Fe.

entropy of αFe by 0.00113, which is equivalent to the entropy of transition $\alpha(=\delta) \rightarrow \gamma$ at 1400°C . Knowing the heat and entropy of transition (ΔH and ΔS), the free energy change of transition is calculated as shown in Table III. While the free energy of transition is very small in the 900° to 1400°C . temperature range, it is fairly large at lower temperatures.

Although valid objections may be raised against the writer's method of obtaining the specific heat of γFe at lower temperatures by direct

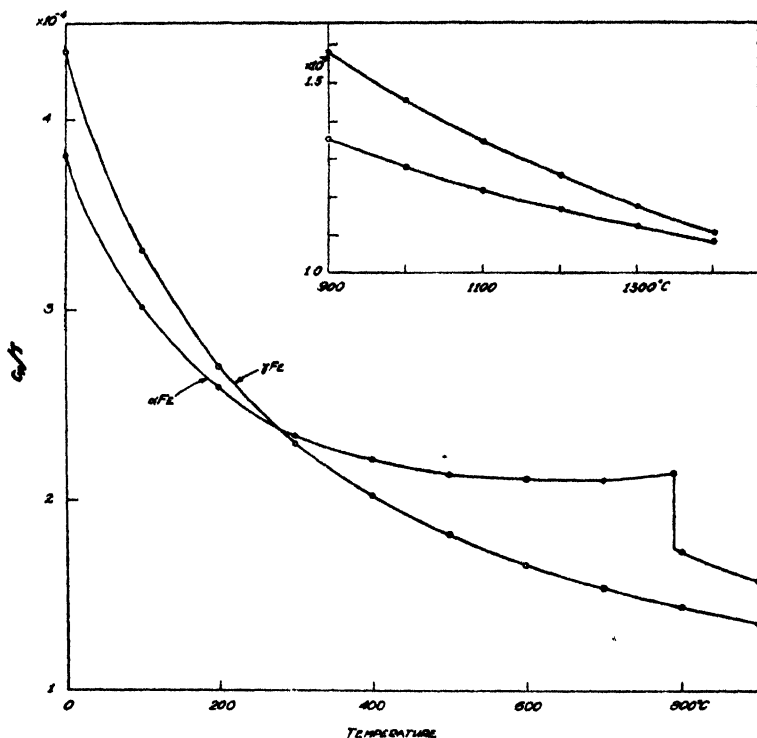


FIG. 4.—The C_p/T values obtained from Table I and Fig. 1 are plotted against T . The relative entropy of α and γFe may be obtained from the area under the curve.

extrapolation, nevertheless, a simple calculation will show that at the most the error in the value of, say ΔF_{298} , cannot be more than 5 per cent. —at higher temperatures the error will be much less. The fact that the specific heat of paramagnetic δFe above 1400°C . is identical with that of αFe below 900°C ., and the fact that the specific heat of γFe (also paramagnetic) is a simple linear function, tend to strengthen the writer's conviction of the validity of his method.

Some Considerations Regarding the Allotropy of Iron.

It is noteworthy that the reversible polymorphism of iron can be formally accounted for by the fact that the absolute entropy of γFe is much larger than that of αFe at lower temperatures. If the heat of transition at 900°C . were larger than 7.6 cal./g., then it is quite conceivable on strictly thermodynamic grounds that the reversal may not

occur,⁹ and that the γ form may remain stable up to the melting-point of iron. This is, of course, tantamount to assuming that the entropy curves shown in Fig. 2 (b) do not intersect each other in the range of 900° C. and the melting-point.

The theory that absolutely pure iron may possess no allotropy may also be examined from the thermodynamic point of view. It was first erroneously assumed by Yensen and others that because no heat evolution (or absorption) was observed at 900° C., that the γ form had been completely suppressed. In order to conceive the γ form to be suppressed, the free energy curve of γ Fe, as shown in Fig. 2 (c), should lie well above the free energy curve of α Fe up to the melting-point. However, to obtain this condition, the heat of transition at A_3 should either become zero or change its sign and the entropy curve of α Fe should lie above that of γ Fe. Looking at Fig. 2 (c), if we move the free energy curve of α Fe downward, we narrow the field of stability of γ Fe (that is, the temperature range between A_3 and A_4), so that eventually the γ form is no longer stable at any temperature. Correspondingly, the heat of transition at A_3 will continually decrease (and even change its sign) while the heat of transition at A_4 increases. Finally, this would require either that the specific heat of γ Fe be diminished or the specific heat of α Fe be increased.

Since from thermodynamic considerations we know that the entropy of a substance in a pure state is smaller than when it is impure (containing dissolved gases or other solutes), the specific heat of α and γ Fe should, therefore, decrease as the purity of the iron increases. In order to suppress the γ form, the decrease in the specific heat of the γ form should be larger than that of the α form. This is not, however, likely to happen, as the effects of impurities are less pronounced in γ Fe than in α Fe, because, in spite of the fact that in γ Fe we have a close-packed structure, it has more solvent power than the latter. On the other hand, it is possible, though not probable, that the specific heat of ferromagnetic iron may be increased as the iron approaches extreme purity, since the sharp increase in the specific heat of ferromagnetic iron is to be attributed to the magnetic component of the specific heat (that is, the thermal energy necessary to neutralise the magnetic moment of the electron spin) and as very pure iron is known to show rather remarkable magnetic properties, an increase in the specific heat might occur.

From considerations such as those given above the writer, in discussing Yensen's paper,¹ predicted that the A_3 point of very pure iron should be well above 900° C., and it has recently been reported that actually the A_3 point is elevated by as much as 35° to 50° C., evidently depending on the extreme purity of the sample. A study of the specific heat of such pure iron is urgently needed.¹⁰

⁹ A point of interest regarding the reversible polymorphism of iron is that the face-centred cubic lattice of pure γ Fe can be expanded to a maximum of 3.68 Å at 1400° C., after which it breaks down to the body-centred cubic lattice. On the other hand, when Fe_3C is dissolved in γ Fe, it distends the lattice, until at saturation of 1.7 per cent. carbon we have again maximum distention of the lattice. It is remarkable that at saturation, the parameter of γ Fe is also about 3.68 Å.

¹⁰ An interesting but qualitative treatment of the reversible polymorphism of iron has recently been made by U. Dehlinger: *Z. Physik*, 68, 535, 1931. He treats the problem from the standpoint of gas degeneracy of the electrons and points out that the free energy of a metal is probably dependent on the outer electrons, which behaves as a completely degenerate gas. In the case of iron, however, on account of the reversal in the allotropic transition, he assumes that the electrons no longer behave as a completely degenerate gas and in this way the free energy curves of the two allotropic forms can cross twice. He then constructed qualitatively the free energy curves, but the values he obtained are too high.

Summary.

1. On the basis of the specific heat of iron, a strictly formal and empirical treatment of the free energy of transition of iron, $\alpha \rightarrow \gamma$, from room temperature to 1400°C . has been given. The free energy of transition at high temperature is very small, but $\alpha = \gamma$; $\Delta F_{300} = 822 \text{ cal./g. atom}$.

Some discussion on the phenomenon of reversible polymorphism and on the possibility of non-allotropy of iron has been included, in the hope that it might be of interest to those engaged in similar studies.

The writer is indebted to various members of the Department of Chemistry, Washington Square College, New York University, for much stimulating discussion, and for their friendly interest.

*Department of Chemistry,
Washington Square College,
New York University,
New York.*

THE FREE ENERGY, ENTROPY AND HEAT OF FORMATION OF IRON CARBIDE (Fe_3C).

BY YAP, CHU-PHAY * AND C. L. LIU.†

Received 8th August, 1932.

Although iron carbide (Fe_3C) plays a very important rôle in the chemistry of steel and cast iron both in the liquid and solid states, no rigorous study of its free energy of formation over a large range of temperature has ever been made. Characteristic of the present confusion is the controversy over the single and double diagram of the iron-carbon system¹ on account of the fact that Fe_3C has been implicitly assumed (without any proof whatsoever) to be *unstable* at all temperatures. Although the conclusion that Fe_3C is unstable, because upon annealing cast iron we obtain graphite, is obviously untenable from a thermodynamic point of view, it is, nevertheless, generally, if not universally, accepted as valid. In order to determine whether or not Fe_3C is actually unstable at all temperatures, we have made a study of its free energy of formation in conjunction with other thermal data (entropy and heat of formation).

In this paper we shall show how a knowledge of the phase diagram of the iron-carbon system enables us to calculate accurately the necessary equilibrium constants of CO/CO_2 mixtures at very high temperatures, from which the free energy of formation of Fe_3C may be obtained. Because of the existence of allotropy and the formation of solid solutions, the iron-carbon system affords us an exceptional opportunity to study the behaviour of solid solutions at very high temperatures.

* Physical Metallurgist-Chemist, New York City, U.S.A.

† Formerly Fellow, Dept. of Chemistry, Washington Square College, New York University.

¹ Throughout this paper, the assumption will be made that the reader is more or less familiar with the iron-carbon diagram. Consult any recent text-book on the phase rule.

The Free Energy of Formation of Fe_3C .

As free energy equations, like ordinary thermochemical equations, can be added or subtracted, the formation of Fe_3C from iron in the presence of carbon oxides, may be conceived as consisting of two reactions :



in which $K_1 = \frac{[\text{CO}_2]}{[\text{CO}]^2}$ and $K_2 = \frac{[\text{CO}]^2}{[\text{CO}_2]}$.

Likewise, with CH_4/H_2 mixtures, the formation of Fe_3C may be conceived to take place as follows :



in which $K_3 = \frac{[\text{H}_2]^2}{[\text{CH}_4]}$ and $K_4 = \frac{[\text{CH}_4]}{[\text{H}_2]^2}$.

Adding equations (1) and (2) and equations (3) and (4), we obtain



It is obvious that if we know the value of K_1 and K_3 in each case, we can easily calculate the value of ΔF°_5 , because the values of K_2 and K_4 are known over a large range of temperature.

Johansson and von Seth² in their important investigation (made incidentally in connection with decarburisation of steels) have obtained the equilibrium constants of carbon oxides in contact with the different phases in the iron-carbon system³ by the so-called "null" method, which is probably the most accurate used in studies of this kind. It is out of place here to discuss at length the advantages and disadvantages of the different methods, since Johansson and von Seth have already so ably stated the advantages of their method. One point which may be emphasised is that their method precludes the probable influence of oxygen, which is undeniably present in Schenck's⁴ and in Takahashi's⁵ experiments. Maxwell and Hayes⁶ have also made an attempt to measure the change in the free energy and heat of formation of Fe_3C at 650° and 700° C., but unfortunately they used 1 atmosphere pressure of CO/CO_2 . The disadvantages of their method have been already discussed by Johansson and von Seth, who used only 0.4 atmosphere total partial pressure of carbon oxides, the rest being made up by nitrogen. Further comments on the work of Maxwell and Hayes will be made later in this paper.

Although theoretically the CH_4/H_2 mixture should be just as good as the CO/CO_2 mixtures, actually it is extremely doubtful if the former can be used to study the equilibria in the austenite solid solution range, since side-reactions are most likely to occur, e.g., formation of hydrocarbons. Below the A_1 temperature, the CH_4/H_2 equilibria with pearlitic steel (in which the Fe_3C crystals are well formed) should be quite reliable.

² *J. Iron Steel Inst.*, **114**, 295, 1926.

³ Depending, of course, upon the temperature and the composition of the steel, one or two phases may exist in equilibrium with each other.

⁴ *Z. anorg. allgem. Chem.*, **167**, 315, 1927.

⁵ *Sci. Repts.*, Tohoku Imp. Univ., **15**, 157, 1926.

⁶ *J. Am. Chem. Soc.*, **48**, 2178, 1926.

If the steel contains Fe_3C in a fairly fine state of dispersion (e.g. sorbitic pearlite) then the CH_4/H_2 and CO/CO_2 equilibria do not give the true equilibrium of reactions and 3 above. Whether any static method will give a true CH_4/H_2 and CO/CO_2 equilibrium is open to serious question.

Johansson and von Seth confined their study of reaction (1) mainly to temperatures above A_1 (720°C.) so that equation 1 no longer applies. They are dealing with γFe saturated with Fe_3C , coexisting in equilibrium with solid Fe_3C and the gas phase. For the sake of avoiding confusion, we shall make all our calculations of ΔF_s with reference to the standard state. We shall arbitrarily (also for convenience) choose pure αFe as the standard state up to the $\alpha \rightleftharpoons \gamma$ transition at 900°C. (A_2) and again from 1400°C. (A_4) up to the melting-point of iron. Between 900° and

1400°C. we shall adopt pure γFe as the standard state, because it is normally stable in this range.⁷

While equation 1 applies to the simple reaction involving the equilibrium of Fe_3C and αFe in the presence of CO_2/CO gas, it cannot be applied to temperatures higher than 720°C. (A_1) on account of the formation of solid solutions. In Fig. 1 (a) we have a part of the iron-carbon diagram above the A_1 temperature. From the phase rule, we know that in the presence of two solid phases (e.g. α and $\gamma\text{Fe}(\text{soln.})$, or $\gamma\text{Fe}(\text{soln.})$ and Fe_3C) and the gas phase, a binary system is monovariant. Hence, if we fix the temperature, the system becomes uniquely defined,

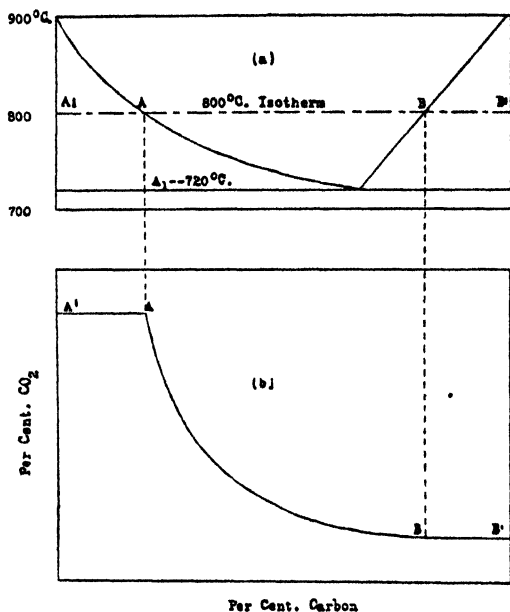


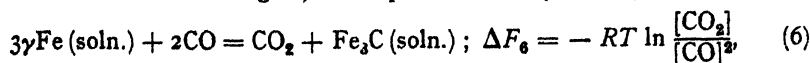
FIG. 1 (a).—Part of the iron-carbon phase diagram. If we plot the percentage of CO_2 in equilibrium with steels of varying composition at, say 800°C. , we obtain (b). Note that the percentage of CO_2 is constant in the heterogeneous fields between A' — A and between B — B' .

that is, the CO_2/CO mixture remains constant, as shown by A' — A and B — B' in Fig. 1 (b). On the other hand, between the composition A and B in Fig. 1(a), since we have only one homogeneous solid phase (solid solution) in addition to the gas phase, the system is divariant and if we fix the temperature (as in Fig. 1) the system still possesses one degree of freedom. Hence, the composition of the austenite solid solution will change; likewise the CO_2/CO gas in equilibrium with the solution.

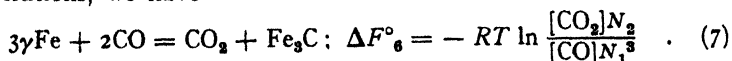
In the composition range of homogeneous solid solutions (i.e. be-

⁷ It will be only reasonable to anticipate that some day we shall refer to the single crystal of a pure substance as the standard state.

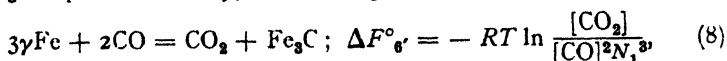
tween A and B in Fig. 1) the equilibrium may be expressed as



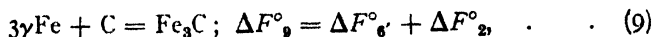
where ΔF_6 is the free energy of reaction. Since we are interested in the change in the free energy of the reaction with every substance in its standard state, equation (6) is easily transformed to the standard free energy equation by introducing the individual activities of the different substances, and so if we consider the activities as proportional to their concentrations, we have



When the solid solution is saturated with Fe_3C and the activity of solid Fe_3C is placed at unity, then the equation reduces simply to



which, combined with equation (2), gives



which is the standard free energy equation for the formation of pure solid Fe_3C from pure solid γFe and carbon, the activities of all of which have been reduced to unity.

It is evident that the calculations of ΔF_9° (*i.e.*, for temperatures above 720°C .) depend upon the accurate determination of the composition of the carbon oxides mixture. The difficulty of obtaining the carbon oxides equilibrium constant at very high temperatures lies in the fact that the percentage of CO_2 is very small. For example, on the basis of the partial pressure of carbon oxides being only 0.4 atmosphere (the rest being nitrogen), the percentage of CO_2 at 1100°C . is only about 0.07. Realising this difficulty, Johansson and von Seth made no attempt to determine the constant. Now, according to equation (6), the constant is given by

$$K_6 = (\text{CO}_2/\text{CO}^2)(N_2/N_1^3),$$

so that, if we plot the CO_2/CO^2 constant against the N_2/N_1^3 constant on a log-log paper, we should obtain a straight line with a positive slope of 1, *provided the austenite solid solutions are ideal, i.e., that they obey Raoult's law*. At the point the locus line cuts the composition represented by B in Fig. 1 (austenite saturated with Fe_3C) the correct CO_2/CO^2 constant is thus obtained for evaluating equation (8). This remarkably simple method depends for its accuracy on the reliability of the phase diagram, giving the solubility curve of Fe_3C in austenite. One of us (Y.C.-P) has recently obtained the A_3 and A_{cm} curves,⁸ which appear to be of very

The data obtained by Johansson and von Seth are only sufficiently high accuracy. complete for the 800°C . isotherm to make a rigorous test of the applicability of our graphical method of obtaining equilibrium constants for equation (8), as shown in Fig. 2. On account of the fact that they did not use pure enough iron-carbon alloys the values equivalent to the A_3 and A_{cm} points shown in Fig. 2 do not quite agree with the value obtained by one

⁸ Soon to be published in the *Trans. Amer. Soc. Steel Treating*.

of us (Y.C.-P.). To be consistent, however, we shall use their value of 0.164 rather than our value of 0.155. Another possible explanation of the discrepancy between their values and ours is that they read their temperatures incorrectly, because on the assumption that the correct temperature was 773° C. instead of 800° C., the two sets of values become more concordant. In spite of the fact that they used only a millivoltmeter to determine the temperature, we prefer, from the internal evidence of the paper by Johansson and von Seth, to attribute the disagreement to the fact that their high-carbon steels were hardly pure iron-carbon alloys.

A study of Fig. 2 shows, we believe, convincingly that only a straight line with an angle of 45° will properly separate the points above and below the equilibrium values. We are therefore justified in concluding that the austenite solid solutions are ideal, at least at the comparatively

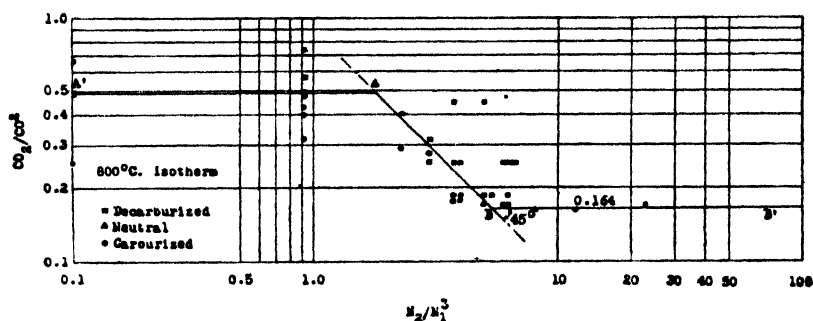


FIG. 2.—The data obtained by Johansson and von Seth have been replotted according to equation (7). This figure is derivative of Fig. 1 (b).

high temperature of 800° C. It is also only reasonable to assume that as the graphical method of obtaining the value of CO_2/CO^2 as shown in Fig. 2 is valid at 800° C., the method should be applicable to higher temperatures, because normally deviations from ideality decrease as the temperature increases. Other values of K_0 (shown in Table II) were thus obtained in the temperature range in which it is practically impossible to determine them directly accurately. In the range up to 900° C., all we need know is one equilibrium CO_2/CO^2 constant in the composition range up to A, whilst in the range above 900° C. the equilibrium CO_2/CO^2 of only one solid solution of a known composition need be determined. It should also be pointed out that the less the concentration of Fe_3C in austenite, the higher the percentage of CO_2 in the carbon oxides mixture, thus materially aiding the accurate determination of the CO_2/CO^2 constant.

Calculations of the Free Energy, Entropy, and Heat of Formation of Fe_3C .

We shall first calculate the free energy of Fe_3C from the CH_4/H_2 equilibria obtained by Schenck and his co-workers⁹ at temperatures below A_1 and the results are shown in Table I, including the values of ΔF_5 . Although the data are probably not of the highest accuracy, nevertheless the final error will be considerably minimised if we also

⁹ *Stahl und Eisen*, 46, 665, 1925.

use their data in calculating the values of K_4 . This is what we have done in Table I, from which we note that Fe_3C becomes less and less unstable as the temperature increases.

TABLE I.—THE FREE ENERGY OF FORMATION OF Fe_3C (ΔF_3) CALCULATED FROM THE DATA OBTAINED BY SCHENCK.

Temp. (°C.).	K_3	K_4	ΔF_3°
360	0.0002939	494.0	2430
445	0.001932	14.60	4932
480	0.01545	4.931	3857
580	0.2702	0.9135	2375
640	0.9645	0.3767	1838
680	2.5375	0.2428	917
700	4.460	0.1928	293
710	4.720	0.1717	408 *
720	6.407	0.1441	174

For temperatures above 720°C . (A_1) we are more concerned with the calculation of ΔF_9° , the free energy of formation of pure Fe_3C from pure γFe and carbon. Since we have already adopted pure αFe as the standard state up to 900°C ., the free energy of transition

$$\alpha\text{Fe} = \gamma\text{Fe}; \Delta F_{10}^\circ \quad (10)$$

is involved. (If we had chosen only pure γFe as the standard state, then it is evident that $\Delta F_{10}^\circ = RT \ln a$, where a is the activity of pure αFe referred to pure γFe at any temperature below 900°C .) In Table II

TABLE II.—THE FREE ENERGY OF FORMATION OF Fe_3C IN THE AUSTENITE (γFe) SOLID SOLUTION RANGE.

Temp. (°C.).	K_3'	$\Delta F_4'$	ΔF_3°	ΔF_9°
750	0.399	1613	— 1606	7
800	0.164	3546	— 3778	— 232
900	0.044	6835	— 7939	— 1104
1000	0.0136	10286	— 12079	— 1793
1100	0.0046	13998	— 16193	— 2195

are shown the values of ΔF_6° obtained according to the graphical method shown in Fig. 2. The values of ΔF_2° are obtained from Eastman's empirical equation¹⁰

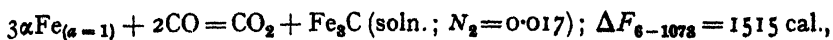
$$\Delta F_2^\circ = 39810 - 10.04T \ln T + 15.32(10^{-3})T^2 - 4.231(10^{-6})T^3 + 6.048(10^{-10})T^4 + 17.12T, \quad (2)$$

which is generally accepted as the most accurate one. Only in the temperature range of 650° to 750°C . is the equation of doubtful value, because no empirical equation can be more accurate than the experimental data on which it is based and the data in that temperature range are not of comparable accuracy, as it is very difficult to establish the true CO_2/CO equilibrium when the volume ratio is 1 : 1. This is because equation 2 is a strictly unimolecular reaction.

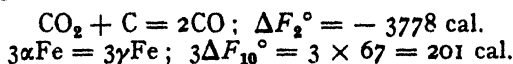
* On the basis of $\Delta F_3 = -RT \ln K_1 K_2$, $\Delta F_3 -_{888} = 421 \text{ cal./mol.}$

¹⁰ Information Circular 6125, Bureau of Mines, May, 1929, pp. 11-12.

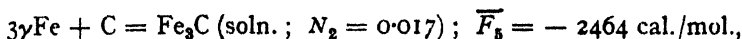
In Fig. 2 we note that the CO_2/CO equilibrium constant in the A'—A range is about 0.4925, that is,



where ΔF_{6-1073} represents the free energy of reaction at $1073^\circ \text{ K. (} 800^\circ \text{ C.)}$, and hereafter it will be omitted as understood. We know that at the same temperature

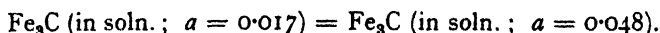


So that combining the three equations gives



\bar{F}_5 being the partial molal free energy of formation of Fe_3C in solid solution.

If we now transfer a mol of Fe_3C from a solution in which its activity (proportional to the concentration) is 0.017 to a solution in which its activity is 0.048, then the free energy change involved is



$$\bar{F}_5 - \bar{F}_5' = RT \ln (0.048/0.017) = 2216 \text{ cal.}$$

$$\text{But } \bar{F}_5 = -2464 \text{ cal.}$$

$$\text{Hence, } \bar{F}_5' = -248 \text{ cal.}$$

Since the austenite solid solution is saturated when 4.8 mol per cent. of Fe_3C is dissolved in it, therefore,

$$\Delta F_9^\circ = \bar{F}_5' = -248 \text{ cal./mol.},$$

which checks almost perfectly the value of $\Delta F_{9-1073}^\circ = -232 \text{ cal.}$ given in Table II.¹¹

Attention is directed to the value of $\Delta F_{10}^\circ = 67 \text{ cal./g. atom}$ used in the calculation of \bar{F}_{5-1073} above. The value of the free energy of transition of iron is taken from another paper by one of us (Y.C.P.) on "The Free Energy of Transition of Iron ($\alpha \rightleftharpoons \gamma$)," also submitted to this society. If we had, therefore, made the calculations backwards, we would have obtained a value of $\Delta F_{10-1073} = 62 \text{ cal./g. atom}$, so that incidentally we now have a check of our value of $\Delta F_{10-1073}$.

In order to show more clearly the change in the values of the different sets of ΔF with respect to temperature, the results are plotted in Fig. 3. Two values obtained by Maxwell and Hayes⁶ are also shown and it is evident that they are incorrect. The high values they obtained are probably due to carbon precipitation, as a result of the high carbon oxides pressure they used. In order to avoid carbon precipitation, they should have used an atmosphere in which the carbon oxides should be 0.4 or less of the total pressure (one atmosphere).

From the fundamental free energy equation, $\Delta F - \Delta H = -T\Delta S$, where $-\Delta S = (d\Delta F/dT)$, that is, the slope of the tangent to the ΔF curve at any temperature. Knowing ΔF and ΔS at any temperature,

¹¹ The negative value indicates that Fe_3C is stable and can form from pure γFe and carbon. It is, therefore, of great interest to note that Sanford [*Bureau of Standards Journal of Research*, 2, 659, 1929] has clearly shown from magnetic analysis that a piece of malleable cast iron, in which the carbon is in the form of graphite, shows the A_2 at 215° C. after it has been previously heated seven times to 800° C. The A_2 is the Curie point of Fe_3C and corresponds to the A_1 point in pure iron.

we can calculate ΔH , the heat of formation. Since below 900°C . we refer to pure αFe as the standard state, we may convert values of ΔF_9 below that temperature by simply adding $3\Delta F_{10}$, the free energy of transition of $\alpha \rightleftharpoons \gamma$. The problem of calculating ΔF_{10} , being rather complicated and requiring extended treatment, is reserved for a separate paper.

Although it is admittedly unsafe to extrapolate over such a large range, nevertheless it is worth while (especially in view of the fact that we have other ways of checking our extrapolated value) to approximate the value of ΔF_{298} , which we find to be around 9300 cal./mol. On the basis of a large-scale drawing, the value of ΔS_{298} is also approximated to be $10.0 (\pm 0.1)$ entropy units. The heat of formation is, therefore,

$$\begin{aligned}\Delta H_{298} &= 9300 + (298 \times 10.0) \\ &= 12280 \text{ cal./mol.}\end{aligned}$$

or simply 12.3 Cal./mol. of Fe_3C .

Watase¹² and Roth¹³ have determined ΔH to be about 2.5 and 3.9 Cal./mol respectively. From general considerations of both the absolute

entropy and the entropy of formation, these values are apparently incorrect, in spite of Roth's reputation for exceedingly accurate calorimetric studies. According to their values, Fe_3C should then be stable at room temperature, which is contrary to facts. The most careful work on the heat of formation at room temperature is probably that by Brodie, Jennings and Hayes¹⁴ who obtained as an average of three values (two very concordant and one evidently incorrect) 13.58 Cal./mol. On the basis of Roth's latest¹³ and apparently more accurate values of

the heat of formation of Fe_2O_3 and Fe_3O_4 , 197.6 and 265.7 Cal./mol. respectively instead of the values of 194.34 and 267.4 Cal./mol. used by Brodie, Jennings and Hayes, their results have been recalculated as follows: 12,366, 13,670 and 12,220 cal./mol. Since the second value differs from the other by more than 1300 cal., and since the two remaining values are very concordant, we shall discard the former and take the mean of the latter values, 12.3 Cal./mol.

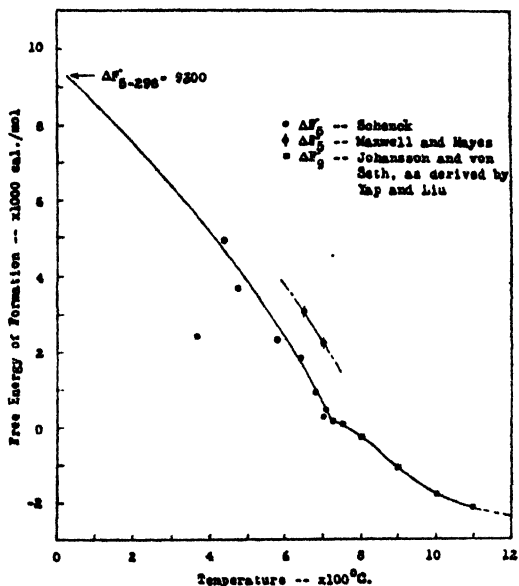


FIG. 3.—The change in the free energy of formation of Fe_3C with respect to temperature. Note that Fe_3C becomes stable above 750°C .

¹² *Sci. Repts.*, Tohoku Imp. Univ., 17, 1091, 1928; also *Z. physik. Chem.*, 147A, 390, 1930.

¹³ *Z. angew. Chem.*, 42, 981, 1929.

¹⁴ *Trans. Am. Soc. Steel Treating*, 10, 615, 1926.

Ruff and Gersten¹⁵ determined the heat of formation to be 15.1 Cal./mol. and later (1913) recalculated it to be 15.3 Cal./mol. Brodie, Jennings and Hayes also recalculated the value obtained by Ruff and Gersten and found it to be about 14.3 Cal./mol. On the basis of Roth's latest values used above, the value of 14.3 may be further reduced to about 13.1 Cal./mol.

Recapitulating, it is more probable from internal evidence that the value of 12.3 Cal./mol. obtained by Brodie, Jennings and Hayes represents the most accurate one to date. The calculated value of ΔH is in perfect agreement with the experimental value, but we could have more confidence in the agreement if we have some means of checking the value of ΔS_{298} . Knowing, however, the absolute entropy of iron to be 16.28 (consult the other paper by one of us, Y.C.—P.) and of carbon to be 5.33, both at 700° C. and accepting $\Delta S = 13.35$ (obtained from the large scale drawing already referred to), the absolute entropy of formation is therefore

$$\begin{aligned} S_{298} &= (3 \times 16.28) + 5.33 + 13.35 \\ &= 67.5 \text{ entropy units.} \end{aligned}$$

From the change in the specific heat curve of Fe_3C with respect to temperature, the increase in the relative entropy of the compound from room temperature to 700° C. is, according to Ralston¹⁶ 34.8 entropy units, but checked by us to be 35.7 entropy units. The absolute entropy of Fe_3C is, therefore, $67.5 - 35.7 = 31.8$ entropy units. According to the work of Rodebush and Michalek¹⁷ the absolute entropy of iron at room temperature is 6.87 and the absolute entropy of graphite may be taken as 1.3 (from Lewis and Randall). Hence, the entropy of formation, $\Delta S_{298} = 31.8 - 21.9$, or 9.9 entropy units, which is a good check of the value of 10.0 obtained from the extrapolated curve as shown in Fig. 3.

We still have a method of checking our values of ΔH_{298} and ΔS_{973} . Although the agreement between the two values of ΔF_{983} in Tables I and II may be considered fortuitous, nevertheless, they give us added confidence in believing they are of the correct magnitude. Accordingly, ΔF_{973} is about 540 cal. and accepting $\Delta S_{973} = 13.35$ (the value we used above), the heat of formation at 700° C. is then

$$\begin{aligned} \Delta H_{973} &= 540 + (973 \times 13.35) \\ &= 13530 \text{ cal./mol.} \end{aligned}$$

We also know that

$$\Delta H_{973} = \Delta H_{298} + \int_{298}^{973} (C_{\text{Fe}_3\text{C}} - \Sigma C_{3\text{Fe} + \text{C}}) dT,$$

where C represents the molal heat capacity and is a variable function of temperature. It is also evident that when we integrate the last term separately, we obtain respectively the total heat contents of Fe_3C and of $3\text{Fe} + \text{C}$ from 298° to 973° K. The total heat content of Fe_3C from 25° to 700° C. is 113.1 cal./g. or 20,308 cal./mol. from Umino's¹⁸ data, which Ralston (*loc. cit.*) used in his calculations of the relative entropy of the compound. Accordingly, we shall be consistent only when we also use Umino's results for iron and for graphite, but unfortunately his results on the latter are very erratic and we shall prefer

¹⁵ *Ber.*, **45**, 63, 1911.

¹⁶ U.S. Bureau of Mines Bulletin No. 296, 1929

¹⁷ *J. Amer. Chem. Soc.*, **47**, 2117, 1925.

¹⁸ *Sci. Repts., Tohoku Imp. Univ.*, **15**, 331, 1926.

using Lewis and Randall's equation,¹⁹ $C_p = 1.1 + 4.8 \cdot 10^{-5} T - 1.2 \cdot 10^{-6} T^2$, which integrated between 298° and 973° K. gives 2445 cal./mol. of graphite. The total heat content of iron within the same limits is, according to Umino, 99.8 cal./g. or 5573 cal./mol. The total heat content of $3\text{Fe} + \text{C}$ between the required temperatures is 19,164 cal., so that the change in the heat of formation is, therefore, 20,308 — 19,164 or 1264 cal., which, added to 12,300 cal. (the heat of formation at 25° C.), gives 13,564, which agrees almost perfectly with our value of $\Delta H_{973} = 13,530$ cal./mol. It should be remarked here that although agreement between the different sets of data may be considered somewhat fortuitous, nevertheless we feel confident that our various derived values are as accurate as the existing data warrant.

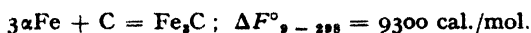
Summary.

1. The theoretical basis of the different free energy equations involved in the calculations of the ΔF and ΔH of Fe_3C has been discussed. The use of αFe as the standard state from room temperature to 900° C. and then above 1400° C. up to the melting-point, and of γFe as the standard state between 900° and 1400° C., has been introduced in order to avoid confusion in our free energy calculations.

2. The theory of CH_4/H_2 and CO/CO_2 equilibria with austenite solid solution and Fe_3C has been discussed.

3. A very simple graphical method of obtaining accurately the CO_2/CO constants at very high temperatures (above $A_1 = 720^\circ \text{C.}$) has been presented. The method gives equilibrium constant of the carbon oxides in the temperature range in which it would be practically impossible to determine accurately by ordinary analytical methods the compositions of the gas mixtures, hence, the free energy change of the reaction.

4. The following important thermal data on the formation of Fe_3C have been obtained:



$$\Delta H_{1000} = 12,300 \text{ cal./mol.}$$

$$\Delta S_{1000} = 9.9 \text{ cal./mol.}$$

$$S_{1000} = 31.8 \text{ cal./mol.}$$

Other values of ΔF and ΔH are also obtained and the change in the value of ΔF , and ΔF_p is shown graphically. The values of ΔH at high temperatures may thus be easily obtained from the relation that $\Delta F - \Delta H = -T\Delta S$ and $d\Delta F/dT = -\Delta S$.

5. From its free energy of formation, Fe_3C is stable above 750°C.

6. It has been shown incidentally that a solid solution like austenite does behave as an ideal solution from the standpoint of Raoult's law. There are good reasons in believing that at high temperatures, many metallic solutions are rather ideal.

Our cordial thanks are due to Professor Cecil V. King, Dept. of Chemistry, Washington Square College, for his discussions and criticism. We are also appreciative of the opportunity of discussing certain phases of this paper with some of the faculty members of the Dept. of Chemistry of the same institution.

*Department of Chemistry,
Washington Square College,
New York University,
New York.*

¹⁹ Lewis and Randall. "Thermodynamics and the Free Energy of Chemical Substances." McGraw Hill Book Co., Inc., New York, 1923, p. 569.

COLLOID CHEMISTRY OF GLUTEN. (BINARY PROTEIN MIXTURES.)

BY H. L. BUNGENBERG DE JONG.

(*Lab. Mij. de Korenschoof, Utrecht, Holland.*)

Received 13th September, 1932.

From the year 1745, when Beccari¹ for the first time described that by washing out a dough, a tough mass of protein remains, this so-called gluten has been one of the principal points of interest for all flour chemists. This interest was based upon the supposition that there must exist some relation between the amount of gluten and the baking qualities of flour.

From a large number of analyses and baking tests it was evident that a positive correlation between protein content and loaf volume exists, but that the coefficient of correlation of protein content and baking strength was widely different for wheats of different variety. These observations are in good accordance with the practical facts obtained with gluten washing. If the glutes of different flours are tested as to their extensibility (often wrongly called elasticity) widely different effects can be observed. A soft flour will give a gluten that can be easily stretched, whereas the hard-flour gluten is brittle and snaps off abruptly. It follows that the gluten of different flours can have a different quality. Accordingly it is now generally accepted that not only the amount of gluten but also its quality plays a leading part in the baking results of the flours (apart from other factors not dealing with the protein).

To a certain extent a lack in total amount of gluten can be compensated by superior gluten quality. To give an exact definition of "quality" is impossible, because this term comprises a large number of widely different physical properties. Several studies have been reported dealing with this quality factor. The first step in this direction was the brilliant work done by Osborne² and his collaborators. These investigators made an end to the confusion about the proteins of flours by proving that gluten consists mainly of only two proteins, gliadin and glutenin.

It is not surprising that a number of chemists have considered the quality of the gluten to be a result of the relative proportions of these two proteins, particularly since the properties of these proteins are absolutely different. Fleurent³ was the first to draw attention to this fact, and he stated in a number of publications that in a good gluten a definite ratio between the two components must exist. A deviation from this ratio would give a gluten of minor quality. There is a distinct lack of agreement among cereal chemists as to the importance of this gliadin to glutenin ratio in connection with baking properties. In the last few years a number

¹ Beccari, cited by Osborne, 1907.

² T. B. Osborne, "The Proteins of the Wheat Kernel," 1907.

³ E. Fleurent, *Compt. rend.*, **123**, 1327, 1896.

of American chemists have pointed out that the gliadin-glutenin ratio varies only slightly between different sorts of wheat. They conclude, therefore, that the differences in the gluten and in the baking qualities of flours cannot be ascribed to the relative proportions of the proteins. Their method of determination of the gliadin is, however, very different from that of Fleurent. In 1929 Berliner⁴ expressed his doubts as to the validity of the American method of gliadin determination. He found a higher gliadin content in different flours, more in accordance with the values determined by Fleurent.

It is necessary before describing our experiments to mention here our final conclusion, *i.e.*, that gluten is not a simple mixture of gliadin and glutenin, but a product formed by an electrical interaction between the two proteins. Therefore it is very doubtful if gliadin and glutenin can be completely separated by the methods of analysis now in use. Now if we are not even sure of the exact ratio of gliadin to glutenin in a flour, it must be quite impossible to pass judgment on the question whether this ratio is one of the factors influencing gluten quality.

Since the analytical methods gave such doubtful results it is no wonder that the chemists have looked for other methods to attack the gluten problem. Of late colloid chemistry has come more and more to the front. In this connection mention may be made of the work of Wood and Hardy⁵ and later of Upson and Calvin⁶ who studied the effects of acids and different electrolytes on gluten. Bailey, Alsberg, Berliner, Gortner, Kent-Jones⁷ and others have contributed their quota to enlarging our knowledge of the gluten properties. However, many of these investigations have been made in a p_H region where the gluten proteins are in an abnormally high state of swelling, or are even completely peptised by the addition of acid or alkali. Although the components of the system are present, the tough complex (characteristic for gluten) no longer exists; in other words the bond between the proteins has for the greater part disappeared.

For this reason we have thought best to study the gluten in that p_H region, wherein the gluten still has its characteristic properties. But already in our first investigations with the raw gluten material we met with difficulties, caused by the complex nature of the gluten. In addition to the proteins gliadin and glutenin quite a lot of other substances can be found in the raw gluten. To avoid these complications and to make our system for investigation as simple as possible, we only studied the effects of the two principal components, gliadin and glutenin, on each other. In doing so we are well aware of the fact that the other components of the raw gluten can have a marked influence on the colloidal properties of the before-mentioned proteins, but we are convinced that the principal properties of the gluten will be found essentially in the protein system, gliadin-glutenin.

Before passing on to the experimental part, it is desirable to mention the following facts. On mixing molecularly dispersed substances there are two possibilities:

(a) The physical properties of the mixture are the sum of those of the components, or

⁴ E. Berliner, *Z. ges. Mühlenwesen*, **6**, 57, 1929.

⁵ T. B. Wood and W. B. Hardy, *Proc. Roy. Soc.*, **B81**, 38, 1909.

⁶ F. W. Upson and J. W. Calvin, *J. Amer. Chem. Soc.*, **37**, 1295, 1915.

⁷ C. H. Bailey, "The Chemistry of Wheat Flour," 1925. Dill and Alsberg, *Cereal Chem.*, **1**, 222, 1924. D. W. Kent-Jones, "Modern Cereal Chemistry," 1927.

(b) There is a deviation from the additive law.

When there is no interaction between the substances, the properties are additive. If the properties are found not to be additive this will indicate that there has been interaction between the components.

The same rules can be applied to the mixing of two colloidal solutions. If the two components do not interact, in other words if, on mixing, the two stability factors of a colloid (charge and solvation) are not changed, a deviation from the rule of additive properties is scarcely probable. This will happen on mixing two protein sols both highly charged, positive or negative. In that case neither the total solvation nor the charge of the particles will be very much influenced. Quite different effects can be expected on mixing two differently charged sols of the same hydrogen-ion concentration. In that case we get in the same solution positive and negative colloid particles. A mutual attraction of the particles followed by a decrease in charge will result. As a consequence a pronounced change in solvation of the mixed system will occur and a pronounced deviation from the rule of additive properties can be expected.

In what range of hydrogen-ion concentration must we look for such a deviation from this rule? Presumably only at those p_H values at which the first component is positive, the other negative. This will only be the case in the region between the iso-electric points of the two proteins. Let us now take for a moment these two sols of opposite charge and at the same p_H . If, on mixing, the charge of the positive component predominates, the total system of the proteins will behave as if it were positively charged. The reverse will take place if the negative protein component is present in excess. In that case the system will react as a negatively charged colloid. Between these two extremes there must be a mixture, which contains an equal number of positive and negative units of charge. Such a system will behave outwardly as if it had no charge. To a certain degree such a zero system (by compensation of the charge of two sols) can be compared with the iso-electric solution of a one-component protein system. In both cases compensation of electric forces takes place. For that reason we conclude that, in the case of a binary system of zero charge by compensation, a maximum or minimum in the physical properties must be found, just as in the iso-electric point of a pure protein. We would emphasize the fact that there most probably exists an equality between the positive and negative units of charge, but not between the quantities of the proteins in such a solution.

Experimental.

Since it was our intention to study the behaviour of gliadin and glutenin and their mixtures in the neighbourhood of their iso-electric points (because here in nature gluten formation takes place) it was impossible to use the viscosimeter. Both gliadin and glutenin are iso-labile and would block up the viscosimeter. Therefore another method (turbidity measurements) had to be followed to get an insight into the charge and solvation of the pure components and of the mixed systems in this p_H region. Turbidity is nearly inversely proportional to viscosity.

The first step was to determine the iso-electric point of both the gluten proteins; this was the more necessary, since in the literature there is a large divergence of opinion as to the iso-electric point of glutenin.

Since electrolytes, such as buffers, have pronounced influence on the iso-electric point, it was necessary to avoid this complication as much as possible. The following procedure was therefore followed. Acid and alkaline solutions of the same protein concentration were made. By mixing these two sols in different proportions solutions were obtained with widely different turbidities, although the total protein concentration was the same in all the tubes. Turbidity measurements were made and afterwards the p_H values of the solutions were determined with the hydrogen electrode. As the solutions were practically free from electrolytes and no buffers were present, it was difficult to get accurate results.

TABLE I.—DETERMINATION OF THE ISO-ELECTRIC POINT OF GLIADIN AND GLUTENIN WITHOUT ANY BUFFERS.

Gliadin.		Glutenin.	
p_H .	Per Cent. Turbidity.	p_H .	Per Cent. Turbidity.
9.7	3.5	7.8	3
9.15	14	6.76	12
8.5	23.5	6.3	31
7.1	41	5.88	48
6.7	69	5.51	52.5
6.58	89	5.32	54
6.4	86	5.12	50
6.25	70.5	4.58	33.5
6	42.5	4.42	29.5
5.72	35	4.2	17
5.45	17	4.08	10
5.1	6.5		

Table I, Fig. 1 gives one of the series of measurements. These data indicate that in practically electrolyte-free media the iso-electric point for gliadin is about 6.5-6.6 and for glutenin 5.4-5.3.

The value for gliadin is in good accordance with that found by Tague,⁸ but widely different from that found by Hoffman and Gortner.⁹ For glutenin there exists a large divergence between the

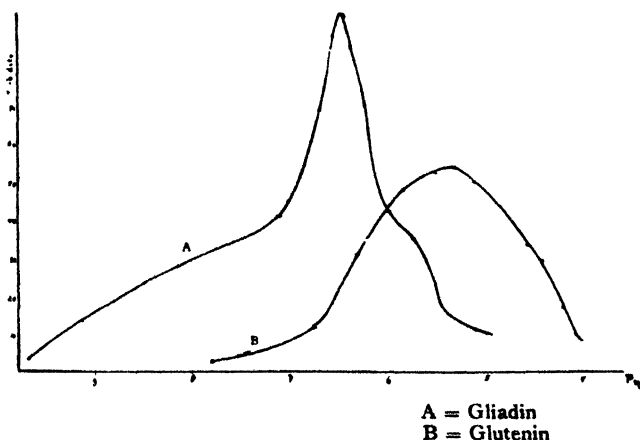


FIG. 1.

values found in our laboratory and those found by Tague and Sharp

⁸ E. L. Tague, *J. Amer. Chem. Soc.*, **47**, 418, 1925.

⁹ W. F. Hoffman and R. A. Gortner, *Colloid Symposium Mon.*, **206**, 1925.

and Gortner.¹⁰ However Kondo and Hayashi¹¹ obtained practically the same value as we found (Table II). In our opinion the value of

TABLE II.

Iso-electric Point of Gliadin.		Iso-electric Point of Glutenin.	
Investigator.	p_H .	Investigator.	p_H .
Hoffman, Gortner .	5.76	Sharp and Gortner .	6.0-8.0
Tague	6.5	Tague	6.8-7.0
Eto ¹²	6.6	Kondo, Hayashi .	5.15-5.39
Lüers ¹³	6.7		
Our laboratory .	6.5-6.6	Our laboratory .	5.3-5.4

Tague and also that of Gortner cannot be correct, for reasons we shall give later (p. 806). On the other hand, we do not wish to maintain that our value 5.4 for glutenin is absolutely right. According to Blish and Sandstedt¹⁴ the molecule will be partly broken up by the action of potassium hydroxide used for the purification of glutenin, which involves a considerable shifting of the iso-electric point to lower p_H values. However, preliminary investigations now being carried out in our laboratory suggest that this shifting of the iso-electric point is caused by quite another factor.

We may expect from the foregoing experiments that, if there were an interaction between gliadin and glutenin, this would take place in a p_H region of about 7 to 5. At lower or higher p_H values a distinct interaction is scarcely probable. This supposition is confirmed by viscosimeter determinations on mixtures of gliadin and glutenin at a p_H of about 3. Table III gives the necessary data, and shows that the viscosity

TABLE III.—RELATIVE VISCOSITY OF GLIADIN-GLUTENIN MIXTURES AT p_H 3.

c.c. glutenin sol .	0	2	4	5	6	8	10
c.c. gliadin sol .	10	8	6	5	4	2	0
Relative viscosity .	1.096	1.116	1.122	1.131	1.139	1.153	1.165
Calc. relative visc. .	—	1.110	1.123 ^b	1.130 ^b	1.137 ^b	1.151	—

of such a mixture is practically directly proportional to the ratio, gliadin-glutenin, and can thus be calculated from the values of the two pure components.

The following method of procedure was used. Known quantities of gliadin and glutenin were dissolved in very dilute sodium hydroxide (0.001 *N.*). These solutions were mixed in varying proportions, but always so that the total amount of protein in the mixtures was a constant. These mixtures were brought to certain p_H values by means of phosphate buffers. Care was taken that the final concentration of

¹⁰ P. F. Sharp and R. A. Gortner, *Minn. Agr. Exp. Stat. Techn. Bull.*, **19**, 1923.

¹¹ K. Kondo and T. Hayashi, *Imp. Univ.*, **5**, 1928, *Chem. Abstr.*, **1**, 1929.

¹² I. Eto, *J. Biochem. (Japan)*, **3**, 373, 1924.

¹³ H. Lüers, *Kolloid Z.*, **104**, 177, 1919.

¹⁴ M. J. Blish and R. M. Sandstedt, *Cereal Chem.*, **2**, 55, 1925.

phosphate was the same for every p_H . Thereupon the turbidity of the solutions was measured.

From considerations of space we refrain from giving all our determinations; only the measurements at p_H 6.1 are given in Table IV. Similar

TABLE IV.—TURBIDITY OF GLIADIN-GLUTENIN MIXTURES AT p_H 6.1.

Per Cent. Glutenin.	Per Cent. Turbidity.	Per Cent. Turbidity Calculated.	Per Cent. Deviation.	Per Cent. Gli. Turb.	Per Cent. Glu. Turb.
0	56	56	100	95 53	66.7 1.5
5	58	53.5	108.4	90 50.5	40 0.75
10	60.5	50.5	119.8	80 45.5	20 0.5
20	61.5	45	136.7	70 41	
30	49	40	122.5	60 35.5	
40	22.5	34.5	65.2	40 23	
60	5.5	23.5	23.4	20 11	
80	4	13	30.8		
90	3	7.4	40.5		
95	2.5	4.7	53		
100	2	2	100		

determinations were made at the other values. In this table column 1 shows the percentage of glutenin in the total protein, column 2 the measured turbidities, column 3 the values calculated according to the law of additive properties, column 4 the percentage deviations from the additive law, columns 5 and 6 the influence on the turbidity of dilution of the pure components.

Fig. 2 (1-7) indicates the influence of changing p_H on the turbidities of mixtures with varying ratio of gliadin to glutenin. In these figures the vertical axis gives the turbidity of the solution, and the horizontal axis the percentage of glutenin in the protein mixture. It is readily understood from these graphs that the ratio of gliadin to glutenin as well as the p_H have an extraordinary influence on the turbidity. At the hydrogen-ion concentration Fig. 2 (1) (about 7) the gliadin can only be slightly negative. For one thing the p_H is very near to the iso-electric point (6.6), and also there are positive ions of the buffer in the solution. Consequently the hydration of the gliadin at this p_H must be very small, and therefore the turbidity of the protein solution is rather high. By addition of a small percentage of glutenin a sharp drop in the turbidity will take place. The glutenin at this p_H is rather strongly negatively charged. This will therefore have a stabilising effect on the gliadin, which is proved by a decrease in turbidity of the solution. It must be well understood that at this p_H both the proteins are negative. Fig. 2 (2-7) are very different; at these p_H values (6.6-5.4) the addition of glutenin always gives, at first, an increase in turbidity, and only at higher glutenin concentrations a decrease. We are here in the p_H region between the two iso-electric points, hence the gliadin is always more or less positively charged. Addition of the first traces of glutenin will give a decrease of charge of the whole system resulting in an increase in turbidity. By increasing the glutenin content of the system a point will be reached, when the number of positively charged units will be compensated by the same number of negative ones. Maximal turbidity will then be reached. By increasing the glutenin concentration still further a surplus of negatively charged protein particles will result,

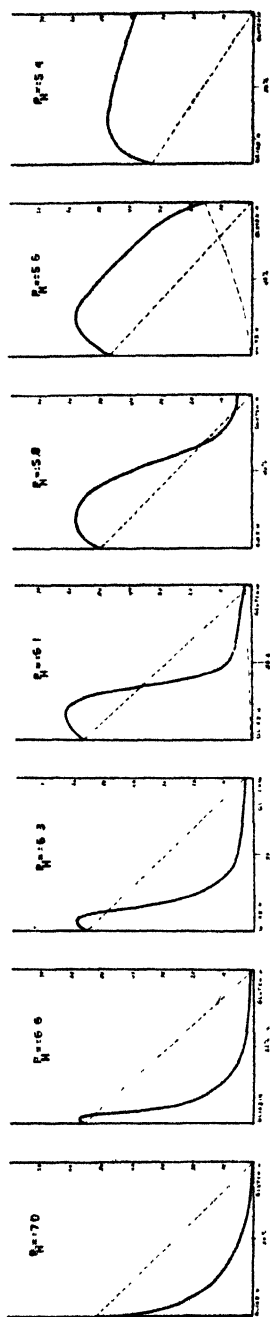


FIG. 2.

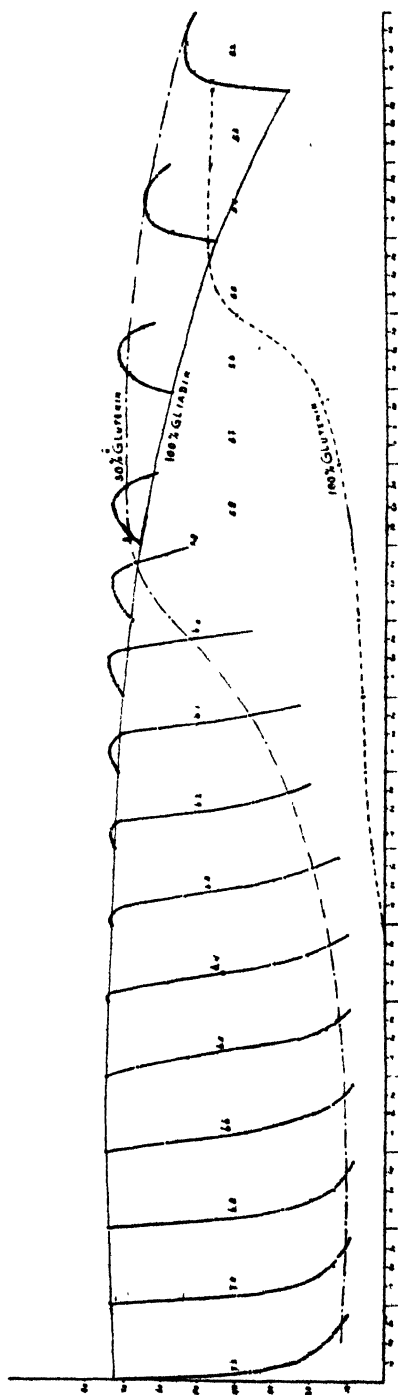


FIG. 4.

causing the system to become clearer and less turbid. By decreasing the p_H of the system a shifting of the maximum to higher glutenin concentrations takes place.

We have already mentioned that a deviation from the law of additive properties indicates interaction between two substances. Therefore the influence of dilution of the pure components on the turbidity was determined at different p_H values. The results are given in Fig. 2 (1-7) in dotted lines. Within the experimental error all the curves are straight lines. It is quite evident that the turbidity found by mixing these two proteins deviates from the additive law. Fig. 3 shows these deviations better; in this the composition of the mixtures is plotted on the horizontal axis, and the percentage deviation * of the additive properties is given on the vertical axis. The turbidities of both the pure components are taken as 100 for simplicity. A dotted line in this figure parallel with the horizontal indicates the pure law of additive properties by mixing. Points above this line indicate a positive, and points below a negative deviation from the additive behaviour of the mixtures. At each p_H between the iso-electric points, positive as well as negative deviations occur, dependent upon the ratio of gliadin to glutenin. Curves F and G provide an exception. Here the deviation is always positive. This graph shows, however, beyond all doubt that there is a distinct interaction between the gliadin and glutenin, at p_H values of about 7 to 5.

The above determinations were made to give a general impression of the effects of the p_H and mixing proportion of

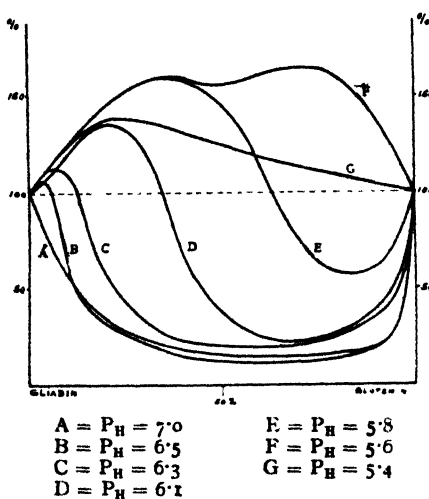


FIG. 3.

the two proteins on the turbidity. The mixtures with 0 to 35 per cent. glutenin were studied more extensively, because in our opinion the glutenin content of gluten must lie somewhere between these percentages. Table V, Fig. 4 gives the results of the measurements. This figure is composed of the turbidity curves for mixtures of 0 to 35 per cent. glutenin at different p_H values. On the horizontal axis the glutenin percentage from 0 to 35 is plotted for every p_H , while the vertical axis gives the turbidities. This graph shows that the first additions of glutenin give a sharp drop in the turbidity of the system at p_H values higher than 6.5. In solutions with a p_H lower than 6.5 an increase in turbidity occurs at first under the same circumstances. Now in a mixture of p_H 6.6 to 6.5 the gliadin is iso-electric, so this graph shows beyond all doubt that the appearance of a maximum in the turbidity curve is coupled with a positive charge of the gliadin. The maximum in the turbidity curves shifts on lowering the p_H to mixtures with a higher glutenin content. In the same graph the curves for the 100 per cent. gliadin and

* Percentage deviation is the value obtained by dividing the values of column 2 by those of column 3 and multiplying by 100.

TABLE V.—TURBIDITY OF GLIADIN-GLUTENIN MIXTURES AT DIFFERENT p_H VALUES.

p_H	Per Cent. Glutenin.								
	5.	10.	15.	20.	25.	30.	35.	100.	0.
7.2	36	23	20	16	14	11.5	9.5	0	72.5
7.0	39	24	18	13.5	13	10.5	9	0	73.5
6.8	45.5	27.5	20	13.5	12	10.5	8.5	0	74
6.6	58.5	37.5	27	19	14	11	8.5	0	74.5
6.5	67	48	35	23.5	16	13	9.5	0	74.5
6.4	72.5	58.5	43.5	30	21	15	10	0	74
6.3	72.5	69	53.5	37.5	27	19.5	12.5	0.5	73
6.2	72.5	73	70	51	35.5	26	18	3.5	72
6.1	72	73	72.5	70	50	36.5	23	5.5	71
6.0	71	72.5	72.5	73	68	52	35	6	70
5.9	69.5	71.5	72	73.5	72	67	59	7.5	67.5
5.8	68.5	70.5	72	73	71.5	69	64	9	65.5
5.7								13	
5.6	65	68.5	69.5	71	71	68.5	65	18.5	57
5.5								40	
5.4	57	62	63	64	64	63	61	47	45.5
5.3								46.5	
± 5.2	46	51	52.5	53	52.5	53	52	46	26

the 100 per cent. glutenin and 30 per cent. glutenin mixtures are drawn by connecting the corresponding points on the turbidity curve for every p_H . The analogous curves for every mixture from 5 to 35 per cent. glutenin are drawn in Fig. 5. In this graph the turbidities of the different gliadin-

Turbidity

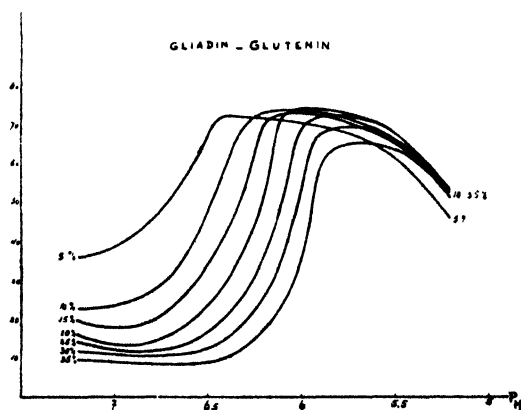


FIG. 5.

glutenin mixtures are plotted against the p_H and it is seen that every mixture has a special p_H for maximal turbidity. Both these graphs indicate that we have to deal with a charge effect.

We will now seek an explanation of these curves. The effects observed are caused by the influence of changing hydrogen-ion concentration on the charge of both the proteins. At p_H 7.2 the gliadin is negatively charged. On lowering the p_H this negative charge will decrease, to become zero at the iso-electric point, p_H 6.5. Beyond this point, down to p_H 5, the positive charge of the gliadin increases. This effect is represented in the 100 per cent. gliadin curve in Fig. 4. The flattened form of this curve is caused by the presence of discharging ions of the buffer in solution. On the other hand, on lowering the p_H from 7.3 to 5.2 the negative charge of the glutenin will decrease, till

its iso-electric point is reached at a p_H of about 5.3. These two effects, the change in charge of both gliadin and glutenin can explain our curves. If we take a mixture with a p_H between the two iso-electric points and decrease the p_H , an increasing amount of glutenin will be necessary to provide an electrical compensation for the positive gliadin and the negative glutenin for maximal complex forming.

The reasons for this are as follows :--

- (a) By decreasing the p_H the positive charge of the gliadin increases.
- (b) By decreasing the p_H the negative charge of the glutenin decreases.

As a result, the maximum in turbidity (found in the mixture wherein the positive units of charge of the gliadin and the negative units of charge of the glutenin compensate each other) will shift to higher glutenin concentrations. For instance, at a p_H 6.2 the gliadin is positively charged. Therefore a certain quantity of negative glutenin (about 7.5 per cent.) will be necessary to compensate this charge of the gliadin to get a maximum complex formation. At another p_H , e.g., 6.0, where the charges of the gliadin and of the glutenin are different, the ratio gliadin to glutenin for maximal complex formation will be different (about 15 per cent.). Considering now Fig. 5, and in particular a mixture containing 20 per cent. glutenin, we find that, with decreasing p_H , the positive gliadin will increase in charge, but at the same time the negative charge of the glutenin will decrease. In this mixture there will

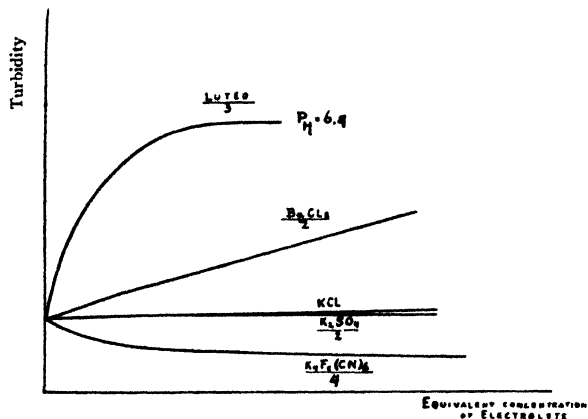


FIG. 6.

be one p_H where the charges of gliadin and glutenin compensate each other (about 6.0). At this p_H no other mixture (e.g., 30 per cent.) can have its maximal turbidity, because here the glutenin percentage is larger and the total negative charge is higher. To reach the maximal turbidity for this mixture, it is necessary to increase the positive charge of the gliadin or to decrease the negative charge of the glutenin. Both these effects can be obtained by bringing the system to a smaller p_H (about 5.8).

The conclusion drawn from these graphs must be that the formation of the complex is closely connected with the charge of both the components. On reasoning thus one would expect that on shifting the p_H to smaller values the maximum of turbidity would shift to ever larger percentages of glutenin. The facts, however, are not in accordance with this supposition. It seems that there is a final value in a medium of this composition for the glutenin quantity of the complex, about 30 per cent. Up to the present we have been unable to give an exact explanation of this fact.

We will now seek to define more closely the connection existing between the formation of the complex and the charge of the system. It

is well known in colloid chemistry that one of the methods of investigating the charge of a colloid is to examine the influence of electrolytes in small concentrations. A colloid is discharged by ions of opposite charge, in the order of their valency. Thus, for instance, the decrease in charge (*i.e.*, a decrease in solvation) of a protein sol will be larger by addition of equivalent concentrations of a tri-valent ion than of a bi-valent one. Such a decrease in solvation of an iso-labile sol is coupled with an increase in turbidity.

Using this method the sign of charge of our binary protein system was tested at different p_H values. For this purpose a sol was made with a gliadin-glutenin ratio of 4:1. The turbidity of this mixture increases on lowering the p_H of the medium until, at p_H 6.1, maximal turbidity is reached. After this point a decrease in turbidity takes place. The influence of different electrolytes on the turbidity of this system was investigated, at, below, and above this maximum, *i.e.*, at p_H 6.4, 6.1 and 5.6. As negative ions Cl^- , SO_4^{2-} and $FeCy_6^{3-}$ were used, while the positive ions were K^+ , Ba^{2+} and $(Co(NH_3)_6)^{3+}$.

The electrolytes with positive ions were all chlorides, while for the negative series potassium salts were used.

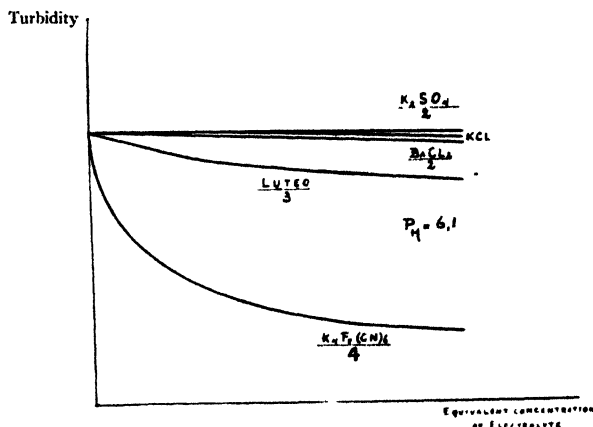


FIG. 7.

will be seen from Figs. 6 and 8. For instance the increase in turbidity at p_H 6.4 was larger for the tri-valent Luteo-ion than for the bi-valent Ba^{2+} ion, and for the Ba^{2+} ion more than for the K^+ ion. For p_H 5.6 the following series was found for the negative ions, *viz.*, $FeCy_6^{3-} > SO_4^{2-} > Cl^-$.

The conclusions from these experiments must be that at p_H 6.4 the negative charge of the system predominates, as indicated by the increased turbidity by addition of positive ions, while at p_H 5.6 there must be an excess of positively charged protein.

So far, there appeared to be nothing abnormal in the conduct of this gliadin-glutenin system under the influence of electrolytes, but the following experiments will make it clear that such a binary-protein system deviates from the type of the ordinary one-component system. If small electrolyte concentrations are added to a charged protein sol, the ions of opposite charge exercise a distinct influence on the solvation of the sol, while ions of the same sign of charge as the colloid are of practically no importance. At the most a small divergency in the turbidity curves can be found between positive sols containing equivalent

The effects found at these three p_H values were quite different. Whereas at p_H 6.4 the positive ions cause an increase in turbidity, at p_H 5.6 the negative ions gave an increase. At both p_H values the turbidity increased in the order of the valency of the discharging ions, as

concentrations of electrolytes with the same negative ion but with varying positive ion.

In a binary system, such as our gliadin-glutenin mixture, quite another effect can be observed. Here also the

ions of the same sign of charge have a distinct influence on the turbidity in the area of complex-formation. In these systems both the ions can change the turbidity. Take, for instance, the gliadin-glutenin sol (8:2) at p_H 6.4. At this p_H the positive ions exercise a perfectly normal influence by increasing the turbidity of the sys-

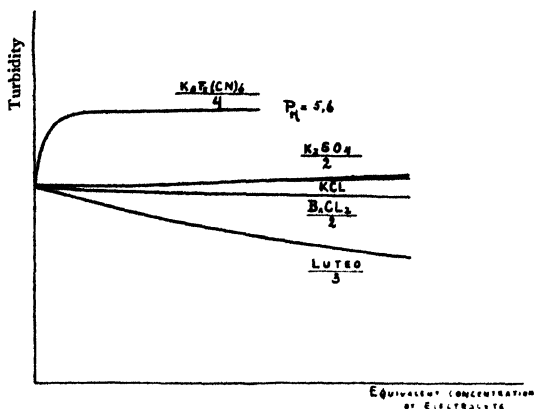


FIG. 8.

tems. The negative ions, on the contrary, give a decrease in turbidity of the system in order of their valency $FeCy_6$, SO_4 , Cl . In the same way at p_H 5.6 the negative ions give a normal increase, while the positive ions give a decrease in turbidity. At p_H 6.1, at which this mixture has its maximal turbidity, both the negative and positive ions decrease the turbidity, and never give an increase at all (Fig. 7). The influence of the positive and negative ions at the different p_H values is represented diagrammatically in Fig. 9.

These ion effects (resulting in a decrease of the turbidity) seem to be in contradiction with the observations on a one-component system. The following interpretation will, however, make it clear that these

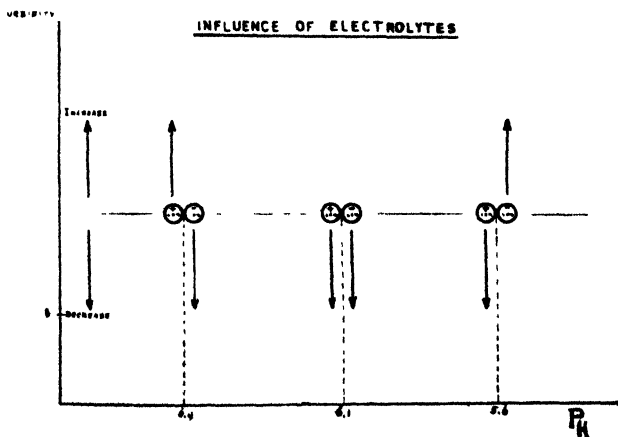


FIG. 9.

effects in a binary system are not indeed anomalous. Let us assume that the complex must consist of positive and negative particles. If this supposition is right, the maximal turbidity must be the result of an electrical compensation of all the positive and negative protein particles.

The so-formed complex will outwardly have a zero charge and therefore a minimum in solvation, but the individuality of both the positive and the negative particles remains, i.e., each of the particles

will be electrically charged according to the p_H and the electrolyte in the medium. (A confirmation of this supposition can be found in the shifting of the point of maximum turbidity along the p_H axis for the different ratios of gliadin-glutenin, Fig. 5). If an electrolyte with a polyvalent positive ion is added, it will be preferentially absorbed and discharge the negative part of the complex. As a consequence the positive part of the complex will not be compensated by a sufficient quantity of negative units. The total system has acquired a surplus of positive charge and a decrease in turbidity will be the result. The same reasoning can be applied to the decrease in turbidity by addition of negative ions in the maximum.*

In analogy with the effects of electrolytes at the maximum (p_H 6.1), the effects of the negative ions at p_H 6.4, and of the positive ions at p_H 5.6, indicate that here, too, some form of a complex must exist. To give a full explanation of the phenomena at both sides of the maximum it is necessary to take into consideration (in addition to the charge of the

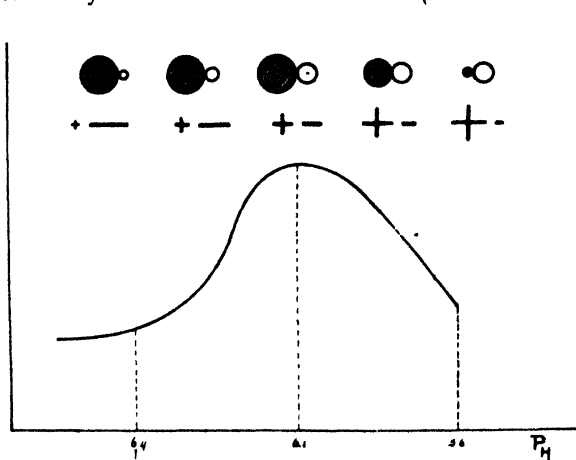


FIG. 10.

charge of the glutenin decreases, until it becomes zero in its iso-electric point. This change in charge of both the components is diagrammatically represented in Fig. 10 by the different size of the positive and negative signs of charge. Moreover in this figure we have tried to give an impression of the ratio of the quantities of gliadin and glutenin in the complex at different p_H values. Here the total amount of the gliadin in the mixture is represented by a large shaded circle, the total amount of the glutenin by a somewhat smaller clear one.

It is easy to understand that at p_H 6.4, where the gliadin is only slightly

* Microscopical cataphoretic measurements support our explanation of the effects of electrolytes. At p_H 6.4 the system is negatively charged. By decreasing the p_H from 6.4 to 6.2 a decrease in the negative charge can be observed. From p_H 6.0 to 5.4 the particles are positively charged as indicated by their motion towards the negative pole. At p_H 6.1 no mobility is shown by the particles.

At the same time the electrical desintegration phenomena—described at length by H. G. Bungenberg de Jong¹⁸ as being an indication of the complex nature of the system—can be found back in the system gliadin-glutenin. So we may safely conclude that the complex consists of positive and negative particles.

¹⁸ H. G. Bungenberg de Jong, *Biochem. Z.*, **221**, 403, 1930.

positive, a very small amount of the highly charged glutenin (± 2.5 per cent.) is necessary to compensate the positive charge of the total amount of gliadin. Therefore the complex must consist of all the gliadin and only a minor quantity of glutenin, as represented in our graph by the large shaded circle for gliadin and the small clear one for the glutenin. As only some few per cents. of the glutenin in the system will participate in the complex formation, a large quantity of this protein will stay in colloidal solution. This part of the glutenin will act as a stabilising colloid for the formed complex and will thus decrease its original turbidity. A simple calculation of the turbidity of the solution by means of the maximum of turbidity will confirm this opinion. On decreasing the p_H , more and more glutenin will be wanted in the complex to compensate the increasing charge of the gliadin, the more so because the glutenin itself decreases in charge. This effect will be coupled with an increase in turbidity of the system, and probably for the following reasons :

- (1) More protein takes part in the complex formation.
- (2) Less glutenin will act as a stabilising colloid.
- (3) The stabilising effect will be less as a result of the decreased charge of the glutenin.

On lowering the p_H still more, a p_H will eventually be reached at which all the positive glutenin is necessary to compensate the negative gliadin. Maximal turbidity will then be reached (p_H 6.1). After this maximum the tables are turned. Now the total amount of glutenin is in the complex while ever decreasing quantities of gliadin will be wanted to compensate the decreasing charge of the glutenin. It is evident that at this side of the maximum a part of the gliadin is not taken up by the complex and is therefore free to act as a stabilising colloid for the complex. The quantity of this free gliadin varies with the p_H .

If the foregoing idea of the mechanism of the complex formation is correct, then the effects of the electrolytes at p_H 6.4 and 5.6 should be in agreement. The experimental facts show that at p_H 6.4 positive ions in small concentrations increase the turbidity of the system. At p_H 6.4 a large quantity of negative glutenin will not be taken up by the complex ; by addition of positive ions the glutenin in the complex as well as in the outer sphere will be gradually discharged, and therefore more glutenin is wanted in the complex to compensate the positive charge of the gliadin. The system becomes more turbid. The same reasoning but now with the negative ions and the positive gliadin in the surrounding liquid holds good for p_H 5.6.

In other words, on discharging the solutions at both sides of the maximum with electrolytes, a situation can be reached, where the complex contains all the protein, the same as in the maximum. Then the turbidities of these solutions must be of the same order as the maximum of turbidity at p_H 6.1. Apart from some small deviations this is in accordance with the facts (see Figs. 6, 7, 8). The consequence of this reasoning should be that higher concentrations of the polyvalent electrolytes give a decrease in turbidity. In fact, Luteo cobaltchloride in higher concentrations gave a pronounced decrease in turbidity at p_H 6.4. The same is the case for K_4FeCy_6 and K_3FeCy_6 at p_H 5.6.

The influence of the negative ions at p_H 6.4 can be explained as follows : At this p_H these ions decrease the charge of the positive gliadin in the complex. Consequently less glutenin will be wanted for compensation, A decrease in turbidity will thus be the result of two effects :—

- (1) The total quantity of protein in the complex decreases,
- (2) The stabilising effect of the glutenin increases.

The same reasoning can be applied for the influence of the positive ions at p_H 5.6.

Summary.

On examining the results of the experiments, the following conclusions can be drawn: The deviations from the law of additive properties for different p_H values, indicate an interaction between the two proteins gliadin and glutenin. This complex formation is caused by the different charges of the components.

In our opinion the individuality of the charge of both the components remains unchanged in the complex, and only the solvation of the components will be changed. Different phenomena point in that direction (disintegration effects of electrolytes, etc.).

The gliadin part of the complex is always positively charged, while the glutenin always acts as the negative component.

Consequently the effect of complex formation is strictly limited to the p_H region between the iso-electric points of the components. Maximum complex formation takes place at a definite p_H . This p_H is only dependent upon the ratio of gliadin and glutenin in the system, and upon the electrolytes in the systems. In a range of about 0.5 p_H units at both sides of the maximum a kind of complex formation can also take place, but such complexes are imperfect. In these systems a certain amount of one of the components will take part in the complex. The remaining part of this protein serves as a protective colloid for the complex.

Nowhere within the area of complex formation indications were found that gliadin would protect glutenin or the reverse. This can only occur at higher or lower p_H values.

All the facts of the summary point to one thing, *i.e.* :

In a definite p_H region the properties of the binary protein system gliadin-glutenin are not those of a purely physical mixture, but of a complex based on electrical relations.

The complex gliadin-glutenin can be compared in a measure with the natural gluten. For one thing because these proteins form the main part of the gluten, and for another because several investigations—not mentioned here—point in the direction that between p_H 7 to 5 this gluten is not a simple mixture, but a system with pronounced complex relations of an electrical nature.

Of course the different minor components of the gluten can have such an influence in this protein system that the forementioned phenomena could be partly covered up. However, in our opinion only a systematical treatment of these different effects can give in the long run the complete solution of the gluten problem.

The author wishes to thank Professor H. G. Bungenberg de Jong and Miss W. J. Klaar for the advice and assistance they have given him during these investigations.

THE EFFECT OF OXYGEN PRESSURE ON THE CORROSION OF STEEL.*

Communication from U. R. EVANS AND C. W. BORGMANN.

Received 4th October, 1932.

Dr. Lee's high-pressure corrosion data are of value and we welcome publication. It is a little unfortunate that the work could not have been carried to slightly higher pressures, so as to ascertain whether the curve of Fig. 4 becomes horizontal, or commences to descend again. Dr. Lee evidently thinks it would remain horizontal, since he states definitely that "Oxygen in solution does not act as a passifier; its function appears to be simply that of a depolarizer and to some extent that of an oxidizing agent for products of corrosion."

Actually the conditions used are not those most likely to produce inhibition at moderate pressures. Owing to the high penetrating power of chlorine ions, chlorides interfere with inhibition even by powerful inhibitors such as potassium chromate, which must be added in larger amount if chlorides are present than if they are absent.¹ Inhibition by oxygen is more likely to be realized when chlorides are absent. One of the writers² found that electrolytic iron, whirled in distilled water containing oxygen, remained uncorroded, whilst the same iron half immersed in the same water, under stagnant conditions, suffered corrosion. Obviously the motion of the water can produce other effects besides accelerating the supply of oxygen to the surface; it will accelerate the removal of iron ions *from* the surface, but this removal is not likely to produce protection; on the contrary, if precipitation as "rust" occurs at a distance from the surface, the precipitate will be looser and less protective.

Even in the presence of chlorides, oxygen can produce a reduction in the *area* suffering corrosion, if favourable conditions are maintained. The writers³ have studied the behaviour of specimens of iron or steel partially immersed in potassium chloride, with different gases above the liquid. When nitrogen free from oxygen was employed, the corrosion, which was very slight, extended right up to the water-line. If a little oxygen was present, a small unattacked area appeared just below the water-line. When purified air was employed, corrosion was confined to a comparatively small area near the bottom and sides, whilst with pure oxygen the corroded area became smaller still. Nevertheless, although increase of oxygen restricted more and more the corroded area, it greatly increased the amount of corrosion. Under the conditions studied, oxygen was a partial inhibitor in one sense, but an accelerator in another.

As pointed out elsewhere, the writers⁴ do not regard the immunity

* This vol., p. 707.

¹ B. E. Roetheli, and G. L. Cox, *Ind. Eng. Chem.*, **23**, 1084, 1931.

² U. R. Evans, "Corrosion of Metals" (Arnold), 1926 edition, p. 108.

³ *Z. physik. Chem.*, (A), **160**, 194, 1932.

⁴ *Proc. Roy. Soc. (A)*, **131**, 355, 1931.

of the aerated zone as *mainly* due to a *directly formed oxide film*, but rather to the fact that, since the cathodic reaction requires oxygen, the cathodic product, potassium hydroxide, is here present in excess; thus any small amount of iron which commences to pass into solution at the well-aerated part of the specimen will be precipitated in optical contact with the metal, repairing and reinforcing the oxide film already present and stopping the attack; in long continued experiments the contact precipitation may lead to a film thick enough to give interference colours, the *character* of which indicates that the film consists mainly of the hydrated oxide, not the less transparent anhydrous oxide. In Dr. Lee's experiments the anodic and cathodic products (ferrous chloride and potassium hydroxide) are produced at points side by side and will destroy one another, so that the protective mechanism does not come effectively into play.

Although the immunity of the "aerated area" of partly immersed specimens is probably due in the main to the alkali there produced, it is to be noted that the co-operation of oxygen is needed in the precipitation of protective hydrated ferric oxide. Potential measurements by Travers and Aubert⁵ indicate that the passivity normally produced by sodium carbonate solution is not met with if oxygen be excluded.

It must be added that conceivably a body might reduce the "probability" of corrosion commencing, and yet increase the "conditional velocity" of attack (which will be attained *provided that* corrosion starts at all); in such a case, a controversy as to whether the body is an inhibitor or not may resolve itself into a question of definition. Early measurements by one of the writers⁶ rather suggested that sodium carbonate acts, in drop-corrosion, as a substance which reduces the probability of attack and increases the conditional velocity. Further work is, however, clearly needed, and it is hoped, at Cambridge, shortly to measure both the "probability" and "conditional velocity" of corrosion by droplets of condensed moisture in a range of oxygen-nitrogen mixtures.

⁵ *Comptes rendus*, 194, 2308, 1932.

⁶ *J. Soc. Chem. Ind.*, 43, 319 T, 1924.

INERT GAS EFFECTS IN CHAIN REACTIONS.

By H. W. MELVILLE.

Received 7th September, 1932.

In certain chain reactions, particularly thermal oxidations, in which wall deactivation is prominent, it has been shown that the addition of inert gases increases the rate of oxidation. This phenomenon was explained by Semenov¹ on the assumption that the inert gas hinders the diffusion of the chains to the walls, postpones deactivation and therefore increases the length of the chains. It was shown by Semenov that the increase in chain length can be represented by the factor

$$1 + p_X/(p_R + p_{O_2})$$

where p_X , p_R and p_{O_2} are the pressures of inert gas, oxidisable substance and oxygen respectively. This expression was derived from the simple

¹ *Z. Physik.*, 47, 109, 1927; *Z. physikal. Chem.*, 2B, 161, 1929.

assumption that the mean free path of the chains in the gas mixture is inversely proportional to the total pressure. Later work on the phosphorus-oxygen reaction² revealed that this was only a first approximation, the second approximation factor being

$$1 + \mu p_X / (p_R + p_{O_2})$$

where μ is a constant and is inversely proportional to the diffusion coefficient of the chains through the gas mixture.

It has now been found that this second approximation holds valid for a number of chain reactions. The object of the present note is to point out some regularities in the values of μ in different reactions and to show that these regularities are in agreement with the theory so far as it has been developed.

The determination of the value of μ may be carried out in two different ways. In the first, the acceleration of the stable chain reaction velocity may be measured. If R_X and R_0 are the rates with and without inert gas present then μ is given by

$$\mu = \frac{R_X - R_0}{R_0} \frac{p_R + p_{O_2}}{p_X} \quad (1)$$

In the second method μ may be obtained by measuring the lowering of the lower oxidation limit upon the addition of inert gas. In these circumstances

$$p'_R p'_{O_2} = p_R p_{O_2} (1 + \mu p_X / (p_R + p_{O_2})) \quad (2)$$

where p' denotes pressures in absence of inert gas.

The Experimental Data.

The available experimental data for six oxidation reactions are collected in Table I.

TABLE I.—REACTION.

Inert Gas.	H ₂ - O ₂ .		CH ₄ - O ₂ .	PH ₃ - O ₂ .	H ₂ S - O ₂ .	CS ₂ - O ₂ .	P ₄ - O ₂ .
He . . .	0.15	2.3	—	—	—	—	0.13
Ne . . .	—	—	—	—	—	—	0.20
A . . .	1.16	7.3	0.8	0.9	0.59	0.64	0.46
N ₂ . . .	2.35	5.1	1.2	0.3	0.44	0.42	0.37
CO ₂ . . .	2.4	—	1.5	—	—	0.83	0.48
SO ₂ . . .	2.6	—	2.7	—	—	0.92	0.52
CH ₃ (OEt) ₂ . . .	3.0	—	—	—	—	—	—
N ₂ O . . .	4.8	—	—	—	—	—	0.46
CCl ₄ . . .	5.6	—	3.4 *	—	—	—	0.84
CHCl ₃ . . .	6.9	—	3.0 *	—	—	—	0.84

With phosphine³ and phosphorus² the lower limiting explosion pressures were determined by the usual methods at temperatures in the neighbourhood of 15° C. In the case of hydrogen⁴ and methane⁵

* Melville and Ludlam, *Proc. Roy. Soc.*, 132A, 108, 1931.

* I am indebted to Dr. H. W. Thompson for these values.

* Dalton and Hinshelwood, *Proc. Roy. Soc.*, 125A, 294, 1929.

* Thompson, *Trans. Faraday Soc.*, 28, 299, 1932; cf. also Horde and Thompson, *J. Chem. Soc.*, in the press.

* Thompson and Kearton, *J. Chem. Soc.*, 933, 1932.

chain centres in sufficient concentration to produce lower limiting explosion pressures had to be introduced by means of an electric spark. The carbon disulphide explosions had to be initiated by a hot tungsten filament.⁶ Similarly a hot filament was required for the hydrogen sulphide,⁷ the gas mixture in both cases being at about 15° C.

μ for neon and argon in the phosphorus reaction was confirmed by experiments on the stable chain reaction below the lower limit.⁸

The second column under the $H_2 - O_2$ reactions shows the value of μ calculated from the data of Gibson and Hinshelwood⁹ on the stable chain reaction above the upper limit. The available data are given in Table II. and the value of μ calculated from equation (1). Pressures are in mm. Hg.

TABLE II.

Helium.				Nitrogen.			
$p_{H_2 + O_2}$	p_{He}	Increase in Rate.	μ	$p_{H_2 + O_2}$	p_{N_2}	Increase in Rate.	μ
450	300	2.45	2.2	300	50	1.26	(1.6)
450	500	3.91	2.6	300	100	2.40	4.2
300	300	1.75	(1.7)	300	150	3.33	4.6
300	500	3.29	2.3	300	200	4.76	5.6
		Average	2.3	300	250	6.17	6.2
						Average	5.1

Argon.				Water Vapour.			
$p_{H_2 + O_2}$	p_A	Increase in Rate.	μ	$p_{H_2 + O_2}$	p_{H_2O}	Increase in Rate.	μ
300	100	2.84	(5.5)	300	50	1.4	(2.4)
300	200	5.24	6.3	300	100	3.6	7.8
300	500	14.2	7.9	300	200	6.2	7.8
300	700	19.1	7.7			Average	7.8
		Average	7.3				

The value of μ does not remain constant but increases with p_x . Moreover, the μ 's for all gases are considerably greater than those obtained by Thompson at the lower limit. Had the values of μ decreased with p_x deactivation by the inert gas would have been indicated. The opposite tendency seems to point to the kinetics being rather more complex than at the lower limit, the inert gas not wholly functioning in the manner common to the other reactions in Table I.

The abnormally large value of μ for N_2O in the spark experiments for the $H_2 - O_2$ reaction is probably due to the N_2O participating in the reaction for when H_2 and O_2 are sparked in presence of N_2O there is appreciable reaction of the N_2O with H_2 . In fact explosive combination of H_2 and N_2O can be brought about by means of a spark.

⁶ Ritchie and others, *Proc. Roy. Soc.*, in the press.

⁷ Ritchie, private communication.

⁸ Melville and Ludlam, *Proc. Roy. Soc.*, 135A, 315, 1932.

⁹ *Proc. Roy. Soc.*, 119A, 591, 1928.

The values for phosphine are possibly complicated by the fact that deactivation is simultaneously occurring with the inert gas effect. For instance, with argon μ decreases down to about 0.3 as the pressure of argon increases; and with nitrogen, although μ remains fairly constant the value appears to be much too low.

It is interesting to point out here that in the photochemical $\text{H}_2 - \text{Br}_2$ reaction at low pressures where wall deactivation becomes evident¹⁰ the inert gas effect increases in the series He, H_2 , O_2 , HBr, Br_2 , thus falling into line with the results of the oxidation reactions.

Discussion.

Thompson⁶ has made the interesting suggestion that it may be possible to estimate the approximate mass and diameter of the chain carriers by a detailed study of the inert gas effect and so enable plausible reaction mechanisms to be verified. For example, to take an extreme case it might be possible to say whether one of the chain carriers in the oxidation of methane is a heavy peroxide or hydroxylated molecule compared with the highly mobile hydrogen atoms and hydroxyl radicals which are supposed to play an essential part in the $\text{H}_2 - \text{O}_2$ reaction.¹¹

On inspection of Table I. the first striking fact is that the inert gas coefficients for the $\text{H}_2 - \text{O}_2$ reaction are consistently higher than those for any of the other reactions. In order to see how this comes about the approximate expression for μ may be considered. It has been shown¹² that μ is given by *

$$\mu = \frac{\sigma_{AX}^2(I/M_A + I/M_X)^{-\frac{1}{2}}}{\sigma_{AM}^2(I/M_A + I/M_M)^{-\frac{1}{2}}}$$

where σ_{AX} is the sum of the radii of A, the chain carrier and X, the inert gas; and σ_{AM} that of A and M the reaction mixture. The radius of A and of M will be a mean value owing to the existence of two chain propagators and of the two different molecules of the reaction mixture. Similarly M_A and M_M will be mean molecular weights. In spite of these complications, it will be assumed that in the $\text{H}_2 - \text{O}_2$ reaction $M_A = 1$ and $M_M = 2$ and σ_A is the radius of the hydrogen atom. Owing to the small value of σ_A , it will have a relatively small influence on the factor $\sigma_{AX}^2/\sigma_{AM}^2$ so that this will be mainly governed by σ_X/σ_M , which will become large when σ_X is large—this, in turn, making μ large. On the other hand when σ_A is comparable with σ_X and σ_M , as is probably the case with the other reactions, $\sigma_{AX}^2/\sigma_{AM}^2$ will not become so great as σ_M increases. For a similar reason, the range of values of μ from He to CCl_4 —0.15—6.9 will therefore be much larger than is the case with the $\text{P}_4 - \text{O}_2$ reaction, 0.13—0.84.

Turning now to the mass factor in the equation for μ it is seen on substituting the values for M_A and M_M and supposing M_X large a value of 1.5 is obtained again tending to make μ high. With other reactions M_A , M_X and M_M are comparable so that the mass factor will approxi-

¹⁰ Jost and Jung, *Z. physikal. Chem.*, **3B**, 83, 1929. Cf. also Kassel, *Homogeneous Gas Reactions*, p. 243.

¹¹ Bonhoeffer and Haber, *Z. physikal. Chem.*, **137**, 263, 1928.

¹² Melville, *Trans. Faraday Soc.*, **28**, 308, 1932.

* This equation is obtained from equations (2) and (11) in reference 12. The coefficient k in (11) is written out in full since k will vary according to the particular reaction being considered.

mate to unity but perhaps rising slightly above this value as M_X becomes large.

Thus both factors for the $H_2 - O_2$ reaction give high values of μ . The contribution of the OH radical in the $H_2 - O_2$ reaction has been neglected for the sake of simplicity. If OH is taken into consideration it would produce slightly lower values of μ .

Another regularity may be observed in Table I., μ for argon, nitrogen, carbon dioxide and sulphur dioxide decreases in the series H_2 , CH_4 , H_2S , CS_2 , P_4 . That is, as the mass and diameter of the oxidisable molecule increases there is a corresponding decrease in μ for any one inert gas. Now the mass and diameter of A will probably be proportional to M, as one of the chain propagators is supposed to be a highly reactive molecule resulting from the oxidation of the combustible substance. Consequently it would be expected for any given inert gas the factor $\sigma_{AX}^2/\sigma_{AM}^2$ would decrease slightly in the series H_2 to P_4 . For a similar reason the mass factor would also tend to decrease.

Thus the two regularities, larger and greater range of μ for the reactions involving lighter molecules of the oxidisable substance is accounted for by the approximate theory.

Summary.

The effect of foreign gases on six oxidation chain reactions is summarised and discussed, the reactions being the oxidation of H_2 , CH_4 , PH_3 , H_2S , CS_2 and P_4 . Certain regularities in the influence of these gases are pointed out and shown to be in agreement with theory so far as it has been developed. For instance, the inert gas has a greater accelerative influence on those reactions involving the oxidation of light molecules. The available experimental data would appear to indicate, on the basis of these calculations, that the mass of the chain carrier molecules increases with the mass of the molecule of the combustible substance.

The author wishes to thank Dr. E. B. Ludlam for his interest in the paper and the Carnegie Trustees for a scholarship during the tenure of which this work was carried out.

*Chemistry Department,
University of Edinburgh.*

SOME GENERAL CONSIDERATIONS IN CONNECTION WITH THE CHAIN-REACTION THEORY.

BY N. N. SEMENOV.

Received 25th August, 1932.

Physical chemistry, as a science, has been mostly concerned with the study of chemical equilibrium, without having been able to throw sufficient light on the kinetics of chemical reactions. The real domain of physical chemistry lay in the investigation of the state of equilibrium of a system with a distribution of energy according to Maxwell's law in which thermodynamics provides the means of a quantitative control. If we consider chemical processes from the standpoint of thermodynamics,

(*i.e.*, if we think of them as of a series of slowly developing successive states of equilibrium), we are able only to trace the relation between the initial and the final state of the system without, however, being offered any possibilities as to a theory of chemical dynamics in which the object of investigation would consist in tracing the evolution of the process.

Every physico-chemical process is mainly characterised by the fact that the distribution of energy, while the process is going on, no longer follows Maxwell's law, with the result that the parameters of equilibrium—temperature especially—become more or less deprived of meaning. If the deviation from Maxwell's law is not too great (as in the case of thermal conductivity or diffusion, for instance), the conception of temperature can still be maintained by attributing to every point of the space a definite temperature at any definite moment. Substituting, for the rather complex phenomena of deviations from Maxwell's law, the derivative of this local temperature as a function of time and space easily gives the mathematical characteristics of processes of this kind to which later on the term of "quasi-steady" processes will be applied.

Until recently chemical processes were considered to belong to the above group; therefore, the velocity of reaction could be determined as a function of temperature and concentration. According to this conception the speed of a given reaction is an indirect function of the time, depending on the corresponding variations of concentration and temperature.

However, the above view does not seem quite consistent. Even when the velocity of reaction is too small to involve any marked increase in the temperature of the system, the deviation from Maxwell's law can be very considerable, as seen from the following: In order that any two molecules of the initial substance be able to interact they must possess considerable energy of activation, E , by far exceeding the average thermal energy. In other words, the velocity of reaction is characterised only by the extreme end, so to say, the "tail" of the Maxwellian curve.

Each elementary reaction act is accompanied by the liberation of free energy which is concentrated in a few molecules of the chemical products and dissipated only after a sufficiently large number of collisions.

The presence of molecules of high energy generated by the reaction markedly alters the distribution of energy at the "tail" of the Maxwellian curve *i.e.*, the very part on which the velocity of reaction depends. The rest of the curve, it is true, remains practically unchanged, but, as already mentioned, this part is of little interest for chemical kinetics. During the whole process a thermometer immersed in the reaction vessel will continue to record the same temperature as before, because it is by no means affected by the behaviour of a few molecules belonging to the "tail" of the Maxwellian curve; but, on the other hand, the reaction mostly depends on what happens at the end of the curve and not on the records of the thermometer. Thus the thermometer cannot be considered as the proper means to investigate things from a kinetic point of view. The conception of temperature, therefore, never ought to be applied without reservations to characterize chemical processes.

The kinetic chain reaction theory was a first rough attempt made to account for the influence of the above-mentioned deviations from Maxwell's law on the velocity of reaction without having to sacrifice the conception of temperature. The idea was this:

Let us suppose the distribution of energy to follow Maxwell's law,

Then, in the unit time there will take place n_0 elementary reactions due to the collisions of molecules carrying the energy E . The amount of energy Q liberated during each single reaction will remain in the products of reaction during a time-interval τ before it undergoes dissipation. If, at the expense of the excess of their energy, the molecules succeed during the interval τ in activating new molecules of the initial substance, then the primary reaction causes a secondary one and so on, thus involving a chain of reactions.

If by α we denote the probability of the chain continuing, the equation which determines the velocity of reaction will be :

$$\tau \frac{dw}{dt} = n_0 + (\alpha - 1)w,$$

whence

$$w = \frac{n_0}{1 - \alpha} \left(1 - e^{-\frac{1-\alpha}{\tau}t} \right).$$

If the energy of a primary reaction be sufficient to cause two secondary ones, α may happen to become larger than unity. In this case

$$w = \frac{n_0}{\alpha - 1} \left(e^{\frac{\alpha-1}{\tau}t} - 1 \right).$$

As well known, the theory of chain reactions enabled us to understand many reactions of which the behaviour was not quite clear from the standpoint of older theories. The number of reactions thus examined is very large, and we may consider every reaction to be more or less of the chain type.

However, the chain reaction theory is only a rough approximation ; the assumption of n_0 being a function of temperature is not quite correct, inasmuch as the considerable deviation from Maxwell's law alters the value of n_0 . In general, the classification of reactions into primary and secondary ones does not seem consistent. Indeed, we have to deal with an altered distribution of energy, and if only we succeeded in calculating this altered distribution, it would mean the possibility of calculating the velocity of reaction too, but, as this altered distribution, in its turn, is a function of velocity the method leads to very complicated integral equations.

According to the above theory, the rate of dissipation, which as a first approximation is expressed by τ , is a constant whose value varies from one reaction to another ; this constant has about the same fundamental meaning as heat capacity in the theory of equilibrium.

As the existence of swift moving molecules is due to collisions of slower ones, the influence of temperature on the kinetics of chemical reactions perhaps is not so negligible as we have stated above. However, it is easy to prove that, making some appropriate assumptions, slowly proceeding reactions can be imagined in which the velocity does not depend on temperature.

Let us assume an extremely low temperature, so low in fact that practically not a single molecule will carry the energy E sufficient for activation ; let us further suppose a reaction showing marked *ramifications* and denote by δ the probability of a branch appearing in the given link. Now let us suppose that the chain breaks up when two active molecules meet (as is often the case when the active centres are formed by atoms whose recombination leads to a breach of the chain). The probability of the chain breaking up will be $\beta = \beta_0 n$, where n is the number of active centres in unit volume. Then $\alpha = 1 + \delta - \beta_0 n$.

On the other hand, the velocity of reaction w is directly proportional to n ; in other words, $\alpha = 1 + \delta - \gamma w$, where $\gamma w = \beta_0 n$.

So long as there are no initial centres formed the reaction does not start. The moment a certain amount of centres is generated artificially (by exposure to illumination or electric discharge) the velocity of reaction increases automatically after the corresponding agent has been removed. Then

$$\tau \frac{dw}{dt} = - (1 - \alpha)w = (\alpha - 1)w = (\delta - \gamma w)w,$$

whence

$$\frac{\delta - \gamma w}{w} = + k e^{-\frac{\delta t}{\tau}},$$

where the value and sign of k depends on the number of initial centres artificially generated at the beginning of the process. Then

$$w = \frac{\delta}{\gamma + k e^{-\frac{\delta t}{\tau}}}$$

The velocity of reaction increases with time approaching the constant value $w = \frac{\delta}{\gamma}$ independently of the number of centres formed initially. Thus we obtain a definite constant velocity of reaction wholly independent of temperature (the values of γ and δ being so).

Some evidence as to the existence of reactions of the above kind is to be found in recent papers.

Haber, Farkas and Harteck,¹ for instance, have shown that after a short exposure to illumination the reaction $\text{H}_2 + \text{O}_2 +$ (and similarly $\text{CO} + \text{O}_2$) continues in the dark during several minutes; in these experiments the mixture of the corresponding gases ($\text{H}_2 + \text{O}_2$, or $\text{CO} + \text{O}_2$) has been taken at 400°C . and sensitised by a slight amount of NH_3 , conditions at which normally the technical process does not proceed at all.

Schumacher and Stieger² noticed a still more surprising fact when studying the dissociation of ClO_2 in the presence of CO ; the explosion of ClO_2 causes the oxidation of CO , the process going on at a slow rate during several days without special exposure to illumination and at a temperature of 45°C . until the whole amount of the gases has combined into CO_2 .

Let us now consider the influence of the second parameter characterising the state of equilibrium, *i.e.* concentration.

The probability of the molecules of the initial substances being activated by the molecules of high energy generated by the reaction during the time these molecules are still keeping their energy decreases as the concentration of the initial substances becomes less and the products of reaction are accumulating. According to the chain reaction theory the probability α is diminishing as the reaction is going on. It follows that, at the state of equilibrium, the velocity of the reaction, both the direct and the compensating reverse one, can decrease many times (and often some thousand times) as compared with that of the initial phase which is far from equilibrium.

The problem of pseudo-equilibrium is thus again put forth on new theoretical foundations. There is no doubt that in practice we often have to deal with the above state of pseudo-equilibrium. For instance,

¹ *Z. Elektrochem.*, **36**, 711, 1930.

² *Z. Physik. Chem.*, **7B**, 363, 1930.

at definite conditions of pressure and temperature, the reactions $H_2 + O_2$, $P_4 + O_2$, etc., proceed with large velocity, being at the same time isothermal reactions. However, they never reach the state of equilibrium, and stop much sooner, when there still remains a somewhat large amount of the initial substances not having yet interacted. Thus, apparently, we ought seriously to reconsider the conception of equilibrium as a state where two reactions are proceeding with large velocity in opposite directions and balancing each other. In most cases the process is unidirectional until a definite moment and practically stops before a fairly good equilibrium has been reached. (Of course, after a sufficiently long time-interval true equilibrium will be established even here.)

There seems to be no reason to extend to all chemical processes the conclusions arrived at for reactions of a decidedly chain character. Nevertheless, the question arises whether the liberation of free energy in a chemical system ought not to be considered as the most important if not the sole agency determining the rate of the reaction; and, further, whether the rôle of any catalyst does not mainly consist in preventing the dissipation of the energy thus generated (by formation of intermediate products, for instance).

The above point of view emphasises the foremost importance of the self-evolution of chemical processes, while other factors (such as temperature, concentration, catalysts and so on) are believed only more or less to help in creating suitable conditions for the action of the chemical forces. In previous theories, on the contrary, these factors were considered to play the principal part.

The new conception of the rôle of free energy in chemical kinetics is somewhat analogous to the question of energy in thermodynamics; it seems very interesting to look also in chemistry for a general kinetic principle similar to that of equilibrium known as the second law of thermodynamics.

My attempts towards this end have not proved satisfactory as yet. I hope there exist no serious objections against the problem being treated in such a general way and would be glad if other workers interested in the theory of the problem attacked it successfully.

REVIEWS OF BOOKS.

Physics. ("Mechanics and Sound," by A. WILMER DUFF, *Editor*. "Wave Motion and Light," revised by R. T. BIRGE and E. E. HALL. "Heat," by C. E. MENDENHALL. "Electricity and Magnetism," by A. P. CARMAN and C. T. KNOPP. Seventh Revised Edition, 1932. London: J. & R. Churchill. Pp. xiv + 681 with 630 illustrations and 44 tables. Price 18s. net.

Intermediate Physics. By C. J. SMITH. (London: Edward Arnold & Co., 1932. Pp. viii + 650. Price 14s. net.

Part I, Fundamental Measurements and the Properties of Matter. Part II, Heat. Part III, Optics. Part IV, Acoustics. Part V, Magnetism and Electricity.

The Ingenious Dr. Franklin. Selected Scientific Letters of Benjamin Franklin. Edited by NATHAN G. GOODMAN. University of Pennsylvania Press and Oxford University Press, 1931. Pp. xi + 244. Price, 15s. net.

This is a fascinating and instructive collection of some of Franklin's letters on scientific subjects. The letters are classified under the heads of Practical Schemes and Suggestions, Divers Experiments and Observations, Scientific Deductions and Conjectures. Assuredly these letters justify the author's choice of a title. It is delightful to read of the small boy using his kite to pull him over a pond and of the man (still with the enquiring and ingenious mind of the boy) experimenting with electricity, with magic squares, and with balloons, making himself bi-focal spectacles and constructing the fore-runner of the Froude tank in order to experiment upon the effect of the depth of water on the speed of boats.

James Clerk Maxwell. A Commemorative volume, 1831-1931. (Cambridge University Press, 1931. Pp. 146. Price 6s. net.)

The volume contains the commemorative addresses delivered on the occasion of the centenary celebrations in Cambridge, amplified somewhat to read as essays. Sir J. J. Thomson in 44 pages tells of the man and of his work; Professor Planck of Maxwell's influence on theoretical physics in Germany; Professor Einstein of his influence on the development of the conception of physical reality. Then Sir Joseph Larmor writes of his scientific environment, Sir James Jeans of the method of the intuitive theoretical physicist, Professor Garnett of his laboratory, and Sir Ambrose Fleming, as one of his most eminent students, fittingly described some memories of the man and of his work.

It is right that so distinguished a collection of essays should be brought together in one volume, and there will be many who will wish to possess it.

Wireless Receivers: The Principles of their Design. By C. W. OATLEY, with a preface by Professor O. W. RICHARDSON. (Methuen's Monographs on Physical subjects. London: Methuen & Co., Ltd. Pp. 7 + 103. Price 2s. 6d. net.)

This admirable little book is in keeping with the other monographs in the series and will be found of general interest to physicists and physical chemists who find it burdensome to follow the special technical (and at times semi-popular) literature to which the bibliography makes reference. All stages of wireless receivers and their essential components are compactly described.

Mathematics. By B. B. LOW. (London: Longmans Green & Co., 1931. Pp. vii + 448. Price 12s. 6d. net.)

The volume is intended for those who are or hope to be engaged in engineering, physics, and chemistry. It covers a wide and sufficient field and is provided with ample exercises for the student.

A History of Fire and Flame. By OLIVER C. DE C. ELLIS. (The Poetry Lover's Fellowship with the International Fellowship of Literature. London: Simpkin Marshall, Ltd., 1932. Pp. xxiv + 436. Price 15s. net.)

Dr. Ellis has at least two calls on his audience. He is known to readers of these *Transactions* as an authority on fire and flame and explosions. He appeals,

however, to a wider field in which he is recognised as a writer of charm and a poet. His book will attract both classes. For the literary minded, scientific fact is clearly explained, and for the sober man of science there is a wealth of information conveyed in language which is, happily, not haunted by the spectre of an adverse publications fund. There are few of us who cannot find joy in a book which is constantly reminding us of things read long ago or of the things we wish now we had read—this line of Virgil, that quotation from Shakespeare. Dr. Ellis' history of flame is fascinating for its facts, but yet more interesting for the scholarliness with which it is written.

It will have been gathered that the book provides no meal for the reader whose history must be predigested and potted or brought into tabloid form. But would such a reader have enough imagination to visualise the interest of the subject? Fire and flame throughout the ages! Dr. Ellis must have had a fascinating time when collecting his materials; fortunately he has the facility to make his readers share his joy.

It would be useless to seek to indicate the contents of the book within a short compass. The chapter headings provide no clue by their recital—the reviewer is still trying to capture the allusion contained in the whimsical heading to Chapter IX. Suffice it to echo the quotations on the dust-cover—"Rich and vivid" says Lascelles Abercrombie; "Every Page aglint with Imagination" says Walter de la Mare. Let there only be added that this is not solely an example of Belles Lettres, but that it is scientifically and historically worth while. It is not merely a history of man's conception of flames, but tells of the uses to which man has thought to put combustion throughout the ages. Perhaps, indeed, the scientific reader will get more enjoyment, even of the literary aspects of the book, than the reader whose technical equipment is lacking. For instance, "Meanwhile Europe was solving its problems in its own way, and that was the employment of the gas which Clayton and Hales had derived from pit-coal by distillation. Like the Chinese natural gas it might be conveyed along pipes, and it would not condense—not all of it."

THE EFFECT OF OXYGEN PRESSURE ON THE CORROSION OF STEEL.

Reply by A. R. LEE to the Discussion by Dr. U. R. Evans and Mr. C. W. Borgmann.¹

Although Dr. Evans and Mr. Borgmann object to my conclusions regarding the function of oxygen in the corrosion process they have not brought forward any conclusive evidence to show that dissolved oxygen can in any way reduce the corrosion of a steel specimen. The result of whirling experiments can be explained similarly to those of Forrest, Roetheli and Brown, without reference to any passifying action of dissolved oxygen.

With regard to the effects of still higher pressures than those considered in Fig. 4 it is already stated in the paper that Chaudron, whose results are in general confirmed by my own, has used pressures up to 120 atmospheres without finding any lowering of the corrosion curve.

I can scarcely imagine that Dr. Evans and Mr. Borgmann are serious when they quote the results of their paper in *Zeitschrift für physikalische Chemie* as evidence that oxygen can produce a reduction in the area suffering corrosion. The photographs in this paper show that under atmospheres of both oxygen and purified air the attacked areas are practically identical and it is evident that in the absence of details of the reproducibility in either atmosphere any attempt to theorise from the difference between these areas would be quite unfounded. They now state that when nitrogen free from oxygen was employed the corrosion "extended right up to the waterline." But in the original paper the corrosion under these conditions was described as showing "only a slight etching and a dark green skin at the waterline; the remainder of the specimen was quite unaltered." In either event, however, the results are in entire disagreement with some recently obtained at Teddington. Here it has been found that with specimens (in a thermostat) half immersed in potassium chloride for about 200 days the area attacked with an oxygen atmosphere may be actually 50 per cent greater than that with purified air.

The experiments of Travers and Aubert did not include any corrosion measurements and have no relevant bearing on the problem of inhibition by oxygen. It has been found experimentally in this laboratory that protection can be produced on a corroding specimen by the so-called "cathodic" alkali at places where there is little or no oxygen in the neighbouring solution.

The concluding remarks by Dr. Evans and Mr. Borgmann centre largely round the definition of an inhibitor, but it is impossible to call oxygen an inhibitor when the rate of corrosion is proportional to the amount of oxygen reaching the metal surface. Localised protection

¹ See p. 813 referring to p. 707.

of a corroding specimen may be produced by the secondary products of the corrosion process, but this protection is exactly compensated by an equivalent increased attack at some other place. The hypothetical "controversy" that is suggested does not arise in the present state of knowledge.

"THE VIBRATORY MOVEMENT" IN FLAMES.

BY OLIVER C. DE C. ELLIS AND E. MORGAN.

Received 16th September, 1932.

Le Mouvement Vibratoire is the label employed by Mallard and Le Chatelier^{1,2} to describe the behaviour of the surface of a flame subsequent to its motion at a sensibly constant speed—*le Mouvement Uniforme*—along a tube that was open at the firing end. It vibrates longitudinally about its steady forward movement, suffering a constant change of area.⁷ At its mean position it is a circular or elliptical disc covering the cross-section of the tube, but while the rim of this disc changes its position with the same order of speed as before, the more mobile portion of the flame surface is whipped rapidly back and forth.

The present paper describes an investigation of the propagation of flame in moisture-saturated mixtures of carbon monoxide and air, from open to closed end of a horizontal tube with particular reference to these vibrations. It is shown analytically that they are determined partly by the dimensions of the vessel and partly by the speed of sound at each point of the gas. The speed of sound in turn varies as the square root of the absolute temperature of the gas.³ We therefore determine the temperature at each point of the gaseous column and we are able to deduce the acoustic properties of the system.

Relative temperature data are found by our Shadow Displacement method. A ray of light is projected transversely through the tube and its deflection is measured. But the law correlating this deflection with the temperature of the gas involves certain physical constants which cannot be determined directly. The temperature gradient which we build up is so far, therefore, only relative.

We now employ a predetermined value for the flame temperature during the "Uniform Movement" period and the absolute temperature at each point of the system is deduced. The temperature gradient throughout the tube can then be completely charted.

The flame temperature employed is determined by the method of the reversal of sodium lines⁴ applied to a stationary flame burning under special conditions. The conditions of burning are chosen so that the stationary flame is identical with a flame that is experiencing the *Mouvement Uniforme*.

In the theoretical section of the paper, the analyses demonstrate that under conditions of constant pressure the flame would propagate at a uniform speed. If, however, we apply a displacement to the system, it is shown that vibrations are set up, and the equations (1), (2), (3) and (4) are deduced. The conditions under which these various equations apply are as follows:—

(1) When the vibrations are of small amplitude they are independent of the speed of propagation. The mean speed of propagation, and the amplitude of the vibrations, remain constant except for the effect of

cooling. The frequency of the vibrations is given by the period equation of C. H. Lees,⁴ viz,

$$\cot n\xi/C_1 = C_2/C_1 \tan \frac{n(L-\xi)}{C_2} \quad (1)$$

where

ξ = distance of the flame from the open end

C_1 = mean speed of sound in the burned gas *

C_2 = mean speed of sound in the unburned gas

$n/2\pi$ = fundamental frequency of the vibrations

L = length of the tube

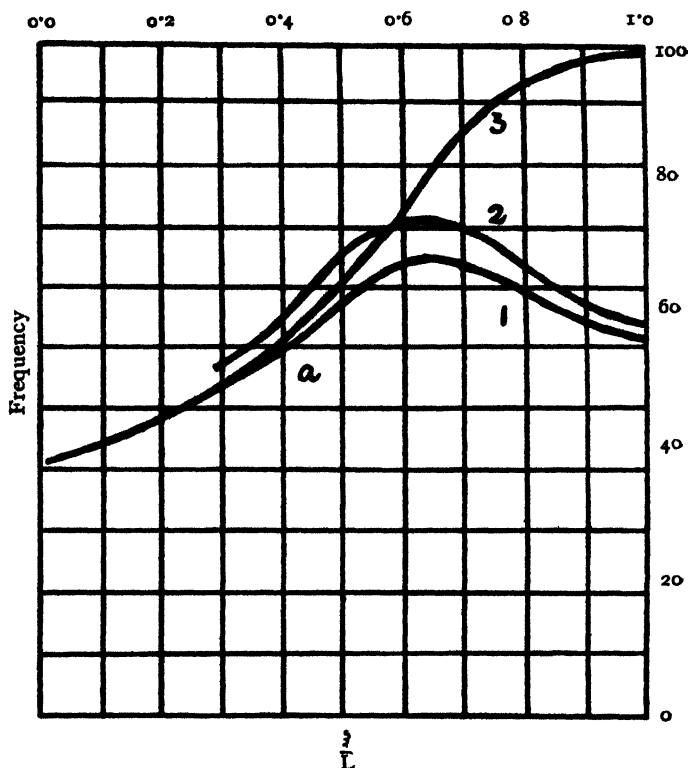


FIG. 1.

(2) When the vibrations are finite their amplitude and the speed of the flame are interdependent. The following relations are obtained.

$$n\xi/C_1 = \pi \quad (2)$$

$$n = \frac{\pi(C_2 + 2C_1)}{2L} \quad (3)$$

$$\frac{A - A_0}{n} = \text{constant} \quad (4)$$

where A is the amplitude of the vibration and A_0 a constant.

* It may be shown by analogy with an organ-pipe that we are justified in taking the mean temperature along the axis. The frequency of the organ pipe is calculated (1) under a linear or exponential temperature gradient, and (2) with the corresponding mean temperature. The difference is less than 3 per cent. Our experimental error in the Shadow Displacement measurements is about 5 per cent.

Analytical and experimental results are compared in Figs. 1 and 2. The experimental results are obtained from photographic records of the flame-propagation in a mixture of carbon monoxide and air containing 25 per cent. CO. The explosion tube was 130 cm. long and 3.5 cm. in diameter. This set of experiments was taken throughout as standard.

The experiments are represented in Curve No. 2 shown in Fig. 1. Curve No. 1 agrees well with this. It has been obtained from our equations (2) and (3) above.

It is an advance therefore, on Curve No. 3, obtained from equation (1) above, the period equation, which does not agree with the experimental curve for values of $\xi/L > a$. At this point the amplitude of the vibrations begins to increase rapidly, and curve No. 3 diverges from the experimental curve. Thus this first approximation should only be used

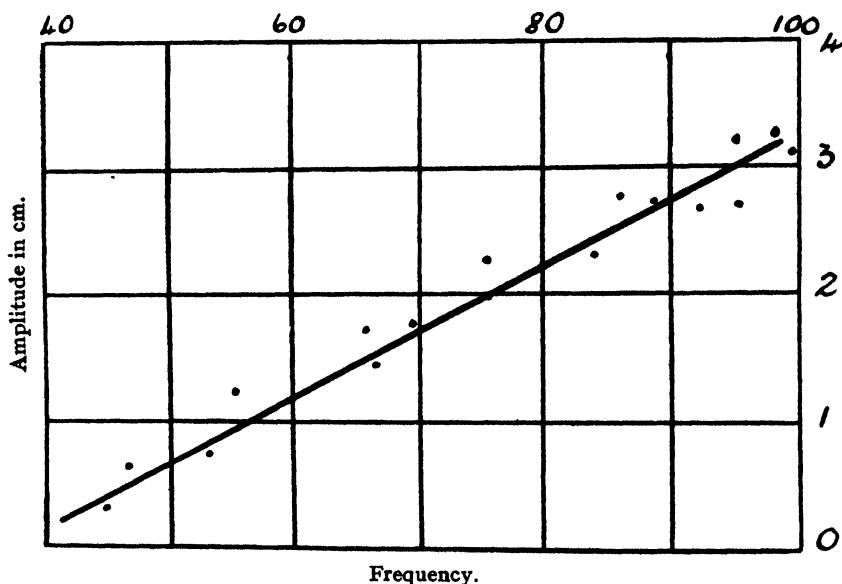


FIG. 2.

whilst the amplitude of the vibrations remains small. The new approximation can be used over the whole range of values of ξ .

In Fig. 2 the straight line relationship between amplitude and frequency obtained in equation (4) is confirmed.

The Shadow Displacement Method.

This method is an adaptation of the ordinary shadow method of photographing regions of discontinuity of density in a gas.⁵ The basis of the method is in the fact that the refractive index of a gas varies with the density according to Gladstone and Dale's Law,⁶ viz.,

$$\frac{\bar{\mu} - 1}{\phi} = \text{constant},$$

where

$\bar{\mu}$ = absolute refractive index.
 ϕ = density.

In the problem under investigation, the pressure is constant and hence the density will be inversely proportional to the absolute temperature θ . Thus

$$(\bar{\mu} - 1)\theta = \text{constant} = (\bar{\mu}_0 - 1)\theta_0 \quad (5)$$

where the suffix $_0$ refers to some set of standard conditions of the gas.

The "lay-out" of the apparatus is shown in Fig. 3.

A diverging pencil of light of angle 8° from the arc lamp A passes through a diaphragm D, of $3/32$ inch aperture, which gives a good point focus. After reflection of the centre ray through 90° at the plane mirror,* the beam passes transversely through the explosion tube and is focussed by the cylindrical lens on to a revolving drum camera. The cylindrical lens is placed with its axis parallel to the axis of the explosion tube and

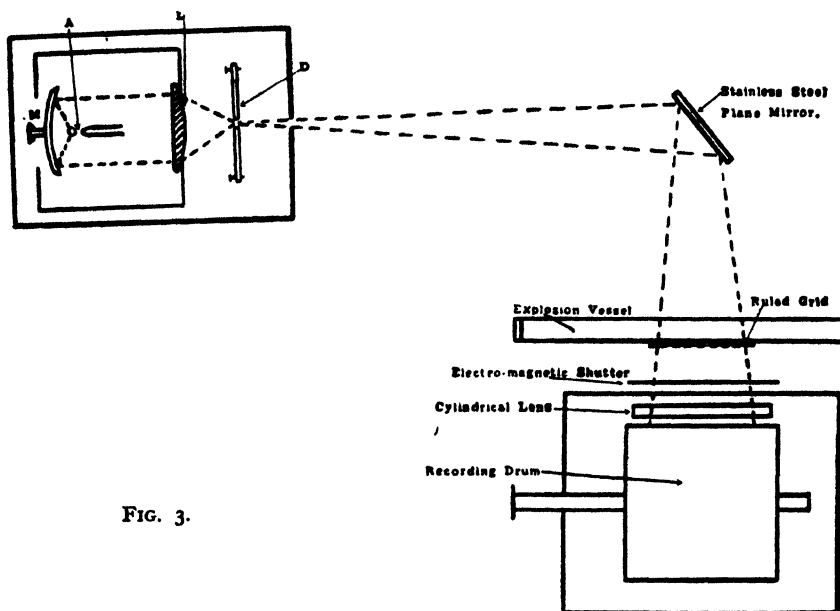


FIG. 3.

serves to give an accurate line image of the walls of the explosion vessel on the drum.

A grid consisting of a set of parallel lines 1 mm. wide, 4 mm. apart ruled on a thin glass plate is placed in contact with the wall of the explosion vessel, the lines being vertical. This produces a set of light and dark bands on the record which are displaced, following law 10 (below), when the flame passes in front of the grid.

The theory of the method is as follows:—

The optical system is shown in Fig. 4. A ray of light incident at an angle i will follow the path ABCDEF.

Then from the optical and geometrical properties of the system it can be shown that the lateral displacement GE of the ray is

$$zt(\tan i - \tan r) + d(\tan i - \tan i_1).$$

* Employed merely to give a compact "lay-out."

Now in the apparatus used the angles i , i_1 , r are less than 5° so that we have approximately

$$\text{Displacement } D = 2t\left(i - \frac{i}{\mu}\right) + d\left(i - \frac{\mu_1}{\mu}i\right),$$

where μ and μ_1 are the refractive indices relative to the glass walls of the explosion tube at the outer and inner surfaces of the tube respectively. The angles are expressed in radians.

The last equation may be written

$$\frac{D}{i} = 2t\left(1 - \frac{1}{\mu}\right) + d\left(1 - \frac{\mu_1}{\mu}\right) \quad . \quad . \quad . \quad (6)$$

The relative refractive index is given by

$$\mu_1 = \mu_G \cdot \bar{\mu} \quad . \quad . \quad . \quad . \quad (7)$$

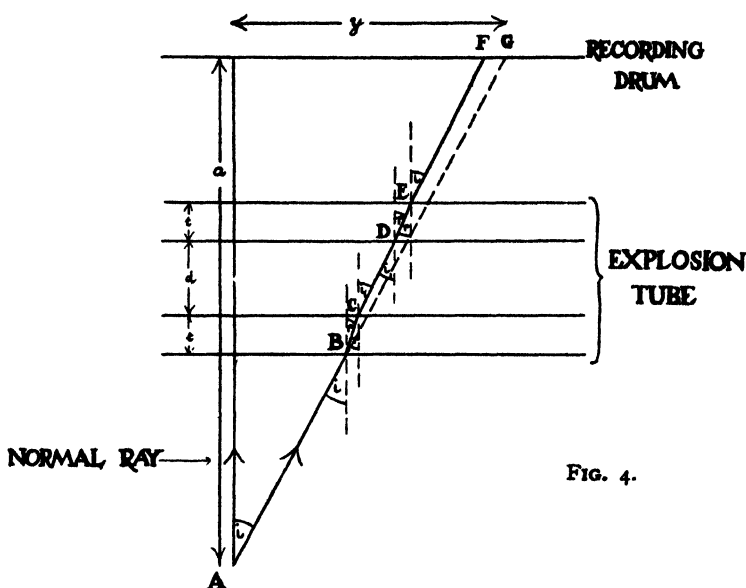


FIG. 4.

where μ_G is the absolute refractive index of the glass walls of the explosion vessel. Combining the equations (5), (6) and (7) we obtain

$$\frac{D}{i} = 2t\left(1 - \frac{1}{\mu}\right) + d\left(1 - \frac{\mu_G}{\mu}\right) - \frac{d\mu_G}{\mu}(\bar{\mu}_0 - 1)\frac{\theta_0}{\theta}.$$

From the figure it may be seen that

$$\tan i = y/a,$$

where a is the distance from the point focus to the drum and y is the distance from the normal ray to the ray under consideration. Since a is constant and i is small, the last equation reduces to

$$i/y = \text{constant} \quad . \quad . \quad . \quad . \quad (8)$$

Finally we obtain the relation between displacement of the ray and temperature of the gas inside the tube

$$D/y = A - B/\theta \quad . \quad . \quad . \quad . \quad (9)$$

where A and B are constants depending on the apparatus and the gaseous mixture within the tube. For a single set of experiments with a fixed explosive mixture they are pure constants. They cannot be calculated directly as they involve certain physical constants, *viz.* μ , μ_0 , μ_θ which are difficult to obtain with a reasonable accuracy. But, as soon as two corresponding pairs of values of D and θ are known their determination is quite straightforward.

These conditions are furnished by the consideration of any point f on the record: (1) In the undisturbed position when the system has cooled to the laboratory temperature θ_0 the displacement may be taken

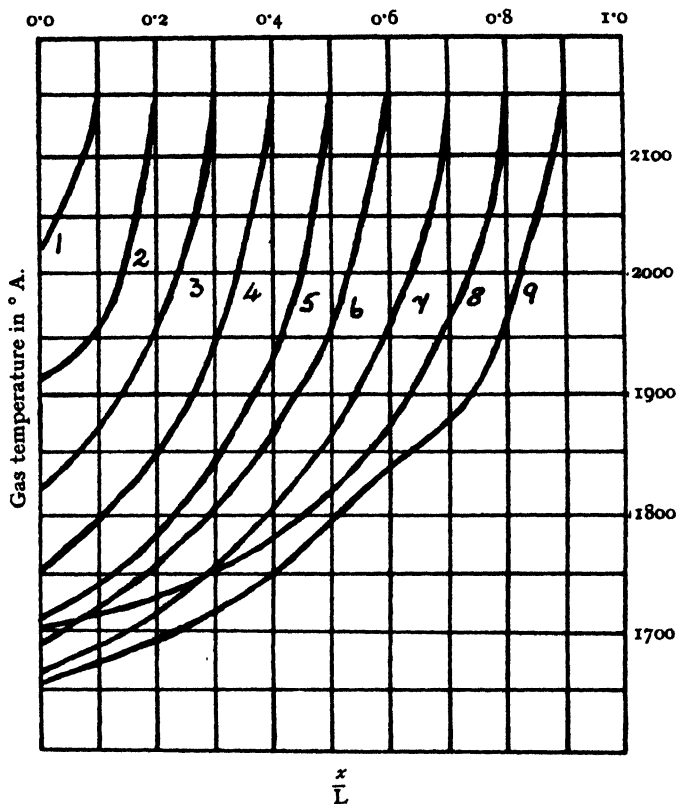


FIG. 5.

to be zero. (2) When the flame during the uniform movement has just passed this point the temperature is θ_f and the displacement D_f .

Putting in these two conditions we have finally

$$1 - \frac{\theta_0}{\theta} = \frac{D}{D_f} \left(1 - \frac{\theta_0}{\theta_f} \right) \quad (10)$$

It would be expected that the flame-front would be the most suitable position for obtaining the calibration values θ_f and D_f . But here a complication is introduced, for the flame-front is curved and the displacement will not follow the law (10).

It is sufficient however for our purpose to assume that the temperature

just behind the flame-front is sensibly equal to that of the flame. This assumption is justified by the results obtained in the measurement of flame temperature by the line reversal method. Thus we may take our standard value of D , as that for the ray which just passes through the burned gas behind the flame-surface without crossing it. The value θ , is the measured flame temperature.

The temperature-gradient along the burned column is continuously changing. The numbered curves in Fig. 5 plot this gradient for nine positions of the flame surface. These nine positions are equidistant at intervals of $L/10$, measuring from the open end. The ratio x/L is the distance-axis, with L , the length of the tube, as the unit of distance.

These curves are obtained for the case of a mixture containing 25 per cent. carbon monoxide and air in a tube 130 cm. long and 3.5 cm. in diameter. In Table I., ξ/L indicates the position of the flame-surface in the tube; the Mean Temperature refers to the burned column; and the velocities of sound are calculated from these mean temperatures.

TABLE I.

Corresponding Curve in Fig. 5.		1.	2.	3.	4.	5.	6.	7.	8.	9.	
ξ/L	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
Mean Temp. °A	2152	2022	1990	1948	1916	1893	1882	1877	1861	1845	1805*
Velocity of sound m/sec.	92.6	91.7	90.6	90.4	90.0	89.7	89.5	89.4	89.2	88.9	88.3

Flame Temperature Determinations.

The measurement of flame temperatures of mixtures of carbon-monoxide and air was based on the reversal of sodium lines as described by Loomis and Perrott.⁸

There were differences between our method and that adopted by Loomis and Perrott. These relate not only to the mixing and delivery of the combustible gas but more especially to the burner used.

In our adaptation, the gas was premixed and delivered in a constant stream from a specially designed gas holder, consisting of a heavy piston falling steadily under its own weight in a cylinder of large bore. The piston was lubricated with high-grade pump oil which provided a steady fall. The flow of gas was adjusted by a needle valve. The stream was passed through a "flame trap"; this consisted of a glass U-tube which had been filled with buckshot: it was tapered at both ends.

The essential difference, however, was in the conditions of burning of the gas whose flame temperature was to be measured. Our burner, shown in Fig. 6, consisted of a specially designed quartz Smithells separator which was placed with the axis vertical. The outer tube was 20 cm. long and of square cross-section, side 2.6 cm. It was necessary to have plane sides to the burner to avoid complications in the lighting system. The

* Extrapolated.

inner tube had a circular section, radius 0.5 cm., and a length 4.5 cm. inside the outer tube. The flow of gas was adjusted so that two definite cones were observed, one burning at the inner tube, the other, outer, cone burning higher up the outer tube.

Measurements of flame temperatures were made at various distances above the tip of the inner cone. It was found that up to a distance of 3.5 mm. from this tip the temperature was sensibly constant. At greater distances, however, the temperature was appreciably lower. For the purposes of our determinations therefore we used the tip of the flame as our standard.

With mixtures containing more than 55 per cent. of carbon monoxide, it was found impossible to control the flow so that a steady inner cone was obtained. The flame floated up and the gas burned in a single cone at the top of the burner.

This burner introduced a further correction to be applied to the temperature determination, namely, the absorption by one wall of the burner. The absorption of two walls was determined by the method applied by Loomis and Perrott for the lens correction at different points of the walls. There was little variation in this correction, 6° being the difference between the greatest and least values of 42° and 36° respectively. The desired correction was therefore half the mean of these two figures namely, 20° to the nearest degree.

Our results are compared with those of Loomis and Perrott in Fig. 7. It will be seen that there are two striking differences.

(1) Our results are consistently higher than those of Loomis and Perrott.

(2) The results for mixtures greater than the maximum speed mixture (35.5 per cent. CO) are entirely different. In our case the slope of the curve is very much less than that of Loomis and Perrott's curve for CO and resembles their curves for hydrocarbons.

The first difference might perhaps have been anticipated from the essential difference in the conditions of burning. In our method, for example, the combustion cannot be influenced by the outside atmosphere. Indeed, we reproduce exactly the same conditions of burning as those obtaining during the "Uniform Movement." The second difference is inherent in the experimental routine. Our results for CO were regular, the mixtures being fully saturated with moisture at laboratory temperature.

The value for temperature obtained was independent of the speed of flow of the gas.

Theoretical.

The theoretical problem of the vibrations cannot be solved exactly. The cooling of the burned gas behind the flame cannot be assessed under a general law. Thus having found temperature data by experiment, we must now deduce the mean value for the whole column of burned

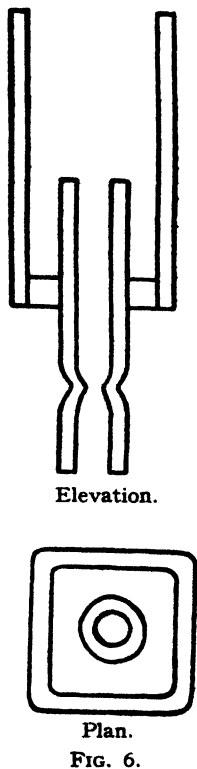


FIG. 6.

gas at each instant. This furnishes us with data sufficient for the application of approximate methods of analysis to calculate the acoustic properties of the system.

We commence the analysis with the two fundamental equations of hydrostatics, *viz.* the Eulerean force equation¹⁰ and the equation of continuity.¹⁰

The first approximation to the motion is obtained by taking the case of constant pressure. By applying suitable boundary conditions at the ends of the tube and at the flame-surface we are led to a steady motion with constant flame speed. Further approximations are obtained by considering the effect of a displacement from the steady motion. If this displacement is very small we may approximate to first order in small quantities. This leads to the period equation (1).

As the flame propagates along the tube, the previous assumptions

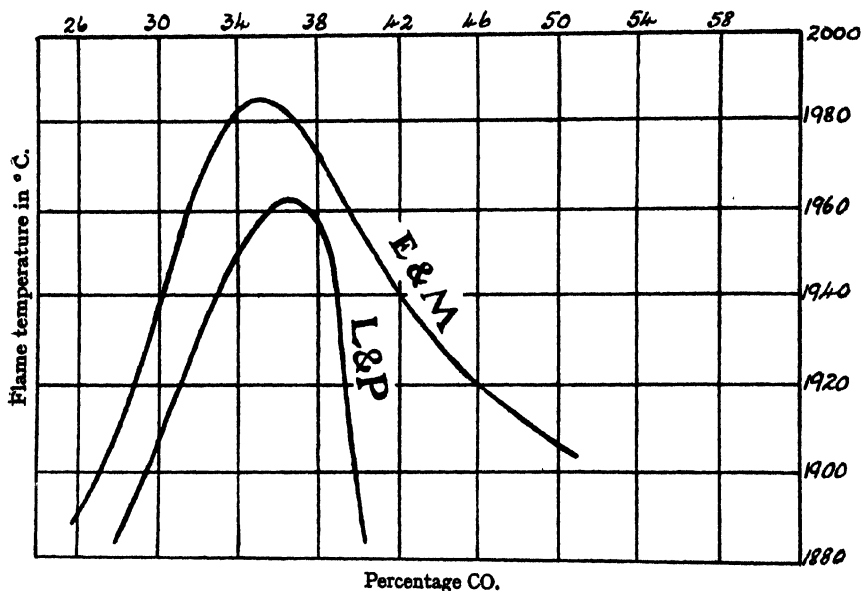


FIG. 7.

become invalid and we consider next the second order of small quantities. At this stage the interdependence of the vibrations and the flame speed is considered. We are led finally to equations (2), (3) and (4).

The motion along the axis of the tube being the only consideration, the cant and curvature of the flame are negligible. (Thus, the cooling effect of the walls—very small in any event⁹ when the diameter of the tube is large—and the action of gravity on the flame are ignored.) The gas is continuous at the flame-surface but the particle velocity is altered by the combustion, *i.e.* the gas moves with a different velocity on each side of the flame-surface.

Since one end of the tube is open to the atmosphere, it is assumed that the mean pressure of the gas remains constant. That is, the only considerable pressure-changes are local and due to the vibrations. It is further assumed that the mass of gas burned per unit time is proportional to the density.

The analysis is as follows :—

Since there are no extraneous forces the Eulerian equation of motion in one dimension in a fluid is

$$\frac{\partial u}{\partial t} + u \frac{\partial u}{\partial x} = -\frac{1}{\rho} \frac{\partial p}{\partial x} \quad . \quad . \quad . \quad (11)$$

where ρ is the density, p the pressure at the point (x) at time t .

The isothermal hypothesis is

$$p = C^2 \rho,$$

where C is the velocity of sound.

Substituting for p the equation (11) becomes

$$\frac{\partial u}{\partial t} + u \frac{\partial u}{\partial x} = -\frac{C^2}{\rho} \frac{\partial \rho}{\partial x} \quad . \quad . \quad . \quad (12)$$

The equation of continuity is

$$\frac{\partial \rho}{\partial t} + \frac{\partial(\rho u)}{\partial x} = 0 \quad . \quad . \quad . \quad (13)$$

The equations (12) and (13) define any gas motion in one dimension.

Steady Motion.

Under these conditions u , $\frac{\partial u}{\partial x}$, etc., are small compared with C^2 and equation (12) becomes

$$\frac{\partial \rho}{\partial x} = 0.$$

Hence, integrating we now have

$$u = -x \frac{\dot{\rho}}{\rho} + f(t) \quad . \quad . \quad . \quad (14)$$

where $f(t)$ is a function of time depending on the initial and boundary conditions.

Consider the case of the motion of a flame surface in a tube length L , the open end at $x = 0$, the closed end at $x = L$. Let the flame have moved to a point $x = \xi$.

$$\text{From (14)} \quad u_1 = v - \xi \frac{\dot{\rho}}{\rho} \quad . \quad . \quad . \quad (15)$$

where v is the particle velocity at $x = 0$;

$$\text{and} \quad u_2 = (L - \xi) \frac{\dot{\rho}}{\rho} \quad . \quad . \quad . \quad (16)$$

$$\text{since} \quad u_2 = 0 \text{ at } \xi = L.$$

Now the mass of gas burned per unit area in unit time is proportional to the density¹¹ and equal to $V\rho_0$ where V is the initial flame speed. Therefore, if A is the cross-section of the tube,

$$A(\dot{\xi} - u_1)\rho_1 = AV\rho_0 = A(\dot{\xi} - u_2)\rho_2, \quad . \quad . \quad (17)$$

and since the pressure is constant,

$$\rho_1 = \rho_0/\lambda \quad \rho_2 = \rho_0 \quad . \quad . \quad . \quad (18)$$

$$\text{where} \quad \lambda = \frac{\text{absolute temperature of burned gas}}{\text{absolute temperature of unburned gas}}.$$

Also the volume increases in the ratio $(\lambda - 1)$ due to burning at the flame surface and this causes a flow of gas with velocity $(\lambda - 1)(\dot{\xi} - u_2)$ out of the open end. Thus it is necessary that

$$v = -(\lambda - 1)(\dot{\xi} - u_2) \quad . \quad . \quad . \quad (19)$$

Eliminating u_1 , u_2 , ρ , $\dot{\rho}$, from (15), (16), (17), (18), (19), we have

$$\text{Hence} \quad \left. \begin{aligned} \dot{\xi} &= V \\ u_1 &= -(\lambda - 1)V \\ u_2 &= 0 \\ \dot{\rho}/\rho &= 0 \end{aligned} \right\} \quad . \quad . \quad . \quad (20)$$

Thus it has been shown in (20), that under conditions of steady motion the flame velocity $\dot{\xi}$ will be constant. This uniform motion will continue until the assumptions on which the analysis is based are no longer satisfied.

Vibrations about Steady Motion.

The cause of the vibrations is the inherent instability of the system. As the flame propagates towards the closed end, the region in which excess pressure is being produced, *i.e.* the flame surface, moves further away from the open end. Thus the action of the open end in releasing the excess pressure becomes less efficient as the flame propagates and the potential energy of the system increases. An increasing potential energy is the criterion for instability. The development of the motion may therefore be obtained by the usual method of applying a displacement to the state of steady motion.

To obtain the new conditions put $u + \sigma$ for u , $\rho + \epsilon$ for ρ in (12) and (13). Then from the results of (20) we shall obtain equations for the displacements σ and ϵ , *viz.* :—

$$\begin{aligned} \frac{\partial \sigma}{\partial t} + (u + \sigma) \frac{\partial \sigma}{\partial x} &= - \frac{C^2}{\rho + \epsilon} \frac{\partial \epsilon}{\partial x}, \\ \frac{\partial \epsilon}{\partial t} + (u + \sigma) \frac{\partial \epsilon}{\partial x} &= - (\rho + \epsilon) \frac{\partial \sigma}{\partial x}. \end{aligned}$$

Initially the displacements σ and ϵ are small and therefore these last two equations may be approximated to :—

$$\left. \begin{aligned} \frac{\partial \sigma}{\partial t} + u \frac{\partial \sigma}{\partial x} &= \frac{C^2 \partial \epsilon}{\rho \partial x} \\ \frac{\partial \epsilon}{\partial t} + u \frac{\partial \epsilon}{\partial x} &= - \rho \frac{\partial \sigma}{\partial x} \end{aligned} \right\} \quad . \quad . \quad . \quad (21)$$

Eliminating ϵ from (21) we have :—

$$\left[\left(\frac{\partial}{\partial t} + u \frac{\partial}{\partial x} \right)^2 - C^2 \frac{\partial^2}{\partial x^2} \right] \sigma = 0,$$

and this is the general equation governing the motion.

The general solution¹² of this last equation is

$$\sigma = f\left(t - \frac{x}{u - C}\right) + g\left(t - \frac{x}{u + C}\right) \quad . \quad . \quad (22)$$

where f and g are functions depending on the initial and boundary conditions.

Now at $x = 0$ there is an open end and the pressure is constant ;
 $\therefore \frac{\partial \epsilon_1}{\partial t} = 0$ for all t .

Hence from (21)

$$u_1 \frac{\partial \sigma_1}{\partial t} + (u_1^2 - C_1^2) \frac{\partial \sigma_1}{\partial x} = 0.$$

This gives

$$\sigma_1 = f\left(t - \frac{x}{u_1 - C_1}\right) + f_1\left(t - \frac{x}{u_1 + C_1}\right) \quad . \quad . \quad (23)$$

Also, at $x = L$ there is a closed end and

$$\sigma_2 = 0 \text{ for all } t.$$

$$\text{Thus} \quad \sigma_2 = f_2\left(t + \frac{L - x}{C_2}\right) - f_2\left(t - \frac{L - x}{C_2}\right) \quad . \quad . \quad (24)$$

First Order Approximations.

When the amplitude of the vibrations is small, then the flame speed u is negligible compared with the speed of sound C .

Thus from (23) and (24) :

If subscripts 1 and 2 refer respectively to the burned and to the unburned gas,

$$\left. \begin{aligned} \sigma_1 &= f_1\left(t + \frac{x}{c_1}\right) + f_1\left(t - \frac{x}{c_1}\right) \\ \sigma_2 &= f_2\left(t + \frac{(L - x)}{C_2}\right) - f_2\left(t - \frac{(L - x)}{C_2}\right) \end{aligned} \right\} \quad . \quad . \quad (25)$$

We now assume a simple harmonic form for the vibrations, *i.e.* we take

$$f_1(z) = A/2 \cos(nz + \alpha) \quad f_2(z) = B/2 \cos(nz + \beta),$$

we have therefore

$$\left. \begin{aligned} \sigma_1 &= A \cos \frac{nx}{C_1} \cos(nt + \alpha) \\ \sigma_2 &= B \sin \frac{n(L - x)}{C_2} \sin(nt + \beta) \end{aligned} \right\} \quad . \quad . \quad (26)$$

Boundary Conditions.

At the flame-surface there are two conditions which must be satisfied. There is a constant difference in pressure on either side the flame-front, and the particle velocity due to the vibrations is continuous.

$$\text{Thus} \quad \left. \begin{aligned} \frac{\partial \epsilon_1}{\partial t} &= \frac{\partial \epsilon_2}{\partial t} \\ \sigma_1 &= \sigma_2 \end{aligned} \right\} \text{ at } x = \xi \text{ for all } t \quad . \quad . \quad (27)$$

Eliminating A , B , α , β between (26) and (27) we obtain the period equation

$$\cot n\xi/C_1 = C_2/C_1 \tan \frac{n(L - \xi)}{C_2} \quad . \quad . \quad (I)$$

Second Order Approximations.

When the amplitude of the vibrations is no longer small the assumption that u may be neglected compared with C^2 is no longer true. We therefore extend the analysis to the consideration of the terms in u/C . Terms containing the square and higher powers of u/C are neglected.

Thus

$$\left. \begin{aligned} \sigma_1 &= f_1\left(t + \frac{x}{C_1}\right) + f_1\left(t - \frac{x}{C_1}\right) + \frac{u_1 x}{C_1^2} \left[f_1'\left(t + \frac{x}{C_1}\right) + f_1'\left(t - \frac{x}{C_1}\right) \right] \\ \text{and} \\ \sigma_2 &= f_2\left(t + \frac{x}{C_2}\right) - f_2\left(t - \frac{x}{C_2}\right) \end{aligned} \right\} \quad (28)$$

The whole gaseous system vibrates with the same frequency $n/2\pi$ at each instant and we assume

$$f_1(z) = A/2 \cos(nz + \alpha) \quad f_2(z) = B/2 \cos(nz + \beta).$$

$$\left. \begin{aligned} \text{Thus} \quad \sigma_1 &= A \cos \frac{nx}{C_1} \left[\cos(nt + \alpha) + \frac{nu_1 x}{C_1^2} \sin(nt + \alpha) \right] \\ \text{and} \quad \sigma_2 &= B \sin \frac{n(L-x)}{C_2} \sin(nt + \beta) \end{aligned} \right\} \quad (29)$$

Consider now the conditions at the flame-surface. As before

$$\left. \begin{aligned} \frac{\partial \epsilon_1}{\partial t} &= \frac{\partial \epsilon_2}{\partial t} \\ \sigma_1 &= \sigma_2 \end{aligned} \right\} \text{ at } x = \xi \text{ for all } t \quad (27)$$

Eliminating A, B, β from (27) and (29) we have:—

$$\begin{aligned} \frac{C_2}{C_1} \tan \frac{n(L-\xi)}{C_2} &= \frac{\cos \frac{n\xi}{C_1} \cos(nt + \alpha) - \frac{u_1}{C_1} \sin(nt + \alpha) \left[\sin \frac{n\xi}{C_1} - \frac{n\xi}{C_1} \cos \frac{n\xi}{C_1} \right]}{\sin \frac{n\xi}{C_1} \cos(nt + \alpha) + \frac{u_1}{C_1} \sin(nt + \alpha) \frac{n\xi}{C_1} \sin \frac{n\xi}{C_1}} \quad (30) \end{aligned}$$

$$\text{i.e.} \quad \frac{C_2}{C_1} \tan \frac{n(L-\xi)}{C_2} = \cot \frac{n\xi}{C_1} - \left(\frac{\sin \frac{n\xi}{C_1} - \frac{n\xi}{C_1} \cos \frac{n\xi}{C_1}}{\frac{n\xi}{C_1} \sin \frac{n\xi}{C_1}} \right),$$

since (30) is true for all t .

$$\text{Thus,} \quad \cot \frac{n\xi}{C_1} = \frac{C_2}{C_1} \tan \frac{n(L-\xi)}{C_2} \quad (1)$$

$$\text{and} \quad \sin \frac{n\xi}{C_1} = 0 \quad (31)$$

Equation (1) is the period equation previously obtained, whilst (31) is a relation which is a necessary condition for the fact that the vibration should remain simple harmonic in character.

UNIMOLECULAR REACTION VELOCITY.

BY M. G. EVANS.

Received 23rd September, 1932.

1. The problem of unimolecular decomposition divides itself naturally into two separate questions. (a) The question of the production of active molecules, and (b) the mechanism whereby these active molecules spontaneously decompose.

It is the second question of spontaneous decomposition with which we propose to deal in this discussion.

Polanyi and Wigner¹ have dealt with the problem as a question of the accumulation of internal energy at some critical degree of freedom in the molecule. In this way the problem becomes a discussion of the probability that in a molecule possessing a total amount of energy E a certain critical amount of the total energy will be concentrated at a special degree of freedom in the molecule.

Polanyi and Wigner have dealt with the special case of a long chain molecule as a classically vibrating system, and have identified the constant A in the well-known equation,² $k = Ae^{-E/RT}$, with some characteristic vibrational frequency of the molecule.

Rice and Ramsperger and Kassel³ have employed the same ideas associating the critical energy with one or two squared terms.

Bourgin and Roginsky and Rosenkewitsch⁴ have considered the problem of decomposition from the standpoint of a non-classical escape through an energy barrier. Criticisms advanced by Kassel⁵ against this treatment are that: "the degrees of freedom not directly concerned in the process seem to pass out of the picture altogether" and "that the energy barrier is of such dimensions that there cannot be any important contribution from such a non-classical escape."

2. Eyring and Polanyi⁶ discussing the mechanism of bimolecular reactions were able, by applying the London method, to construct energy surfaces for the interaction of three univalent atoms. In the case of the hydrogen system $H_2 + H$ it was found, when the coulombic and resonance energies were estimated from Suguira's data, that the energy surface exhibited a shallow hollow of 1.6 kg. cal. deep indicating the formation of an unstable H_3 molecule.

Similar surfaces may possibly be constructed for more complex and unsymmetrical molecules. Fig. 1 shows such an imaginary surface. Escape of the system from the hollow in the surface would represent the unimolecular decomposition of such a molecule. The sections accompanying this figure indicate the various types of vibration in the molecule.

Sections 1 and 2 represent types of vibration in which the distance

¹ *Z. physik. Chem.*, 439, 1928.

² k the velocity constant, E the activation energy, A a constant.

³ For Summary of literature see *Chem. Rev.*, Vol. X., No. 1, 1932.

⁴ Bourgin, *Proc. Nat. Acad. Sci.*, 15, 357, 1929. Roginsky and Rosenkewitsch, *Z. physik. Chem.*, 10B, 47, 1930.

⁵ *Chem. Rev.*, Vol. X., No. 1, p. 22, 1932.

⁶ *Z. physik. Chem.*, 12B, 279, 1931.

AB or BC remains constant while C or A respectively vibrate with respect to the rest of the molecule. Increasing the energy of the molecule and maintaining the same type of vibration, the molecule will occupy successively higher energy levels until finally it decomposes into AB and C or BC and A.

The potential hump in this type of vibration is of such nature that although it need not be high its breadth will not allow the probability

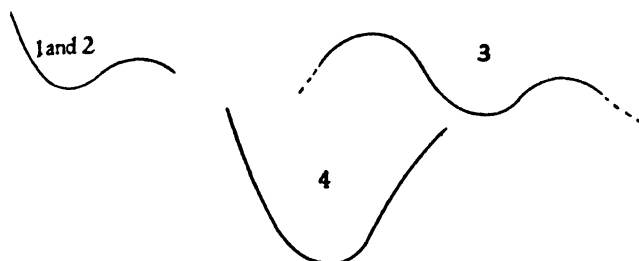
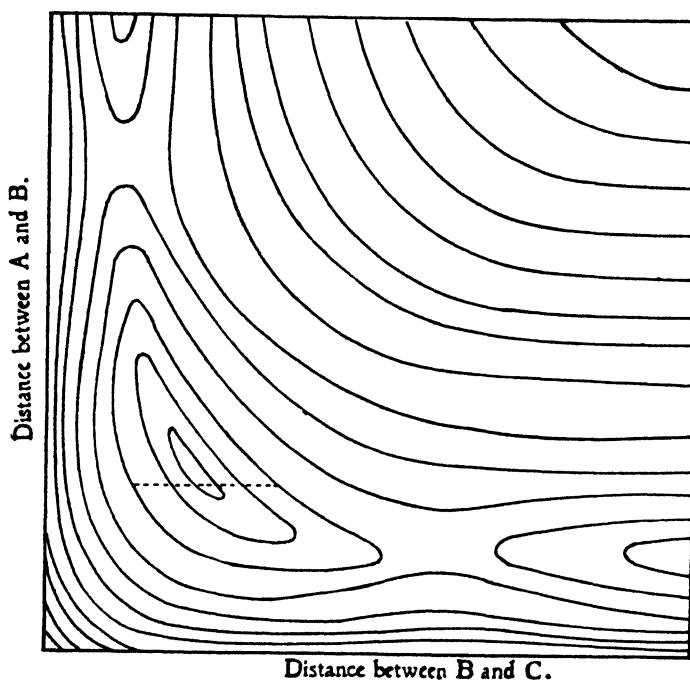


FIG. 1.

of non-classical escape across the hump to be of any importance. Moreover in this case Kassel's⁵ criticism holds that "the rest of the molecule is left out of the picture."

Section 3 represents a type of vibration in which BC is compressed while AB is extended, and at the other extreme AB is compressed while BC is extended. This type of vibration again leads to a final decomposition into AB and C or BC and A.

Section 4 represents a type of vibration in which all the atoms are

extended at one extreme and compressed in the other extreme position.

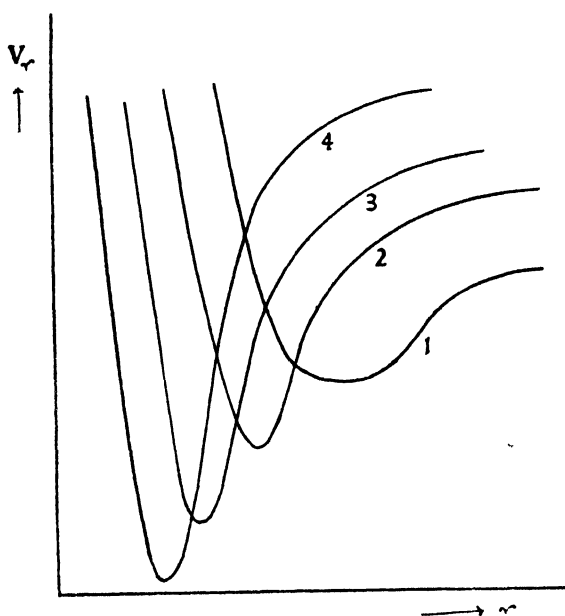


FIG. 2.

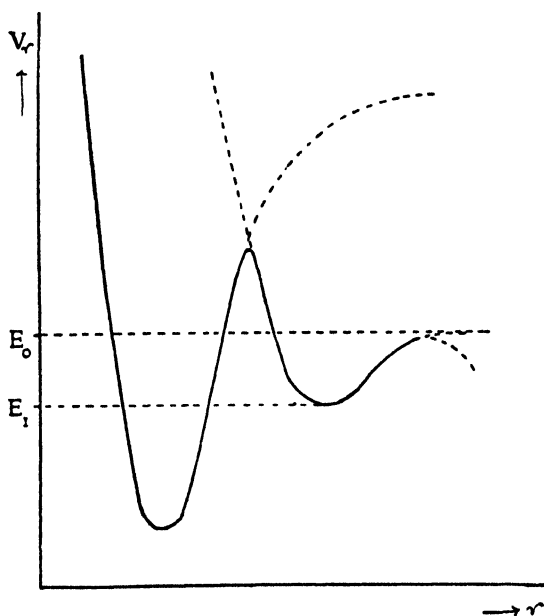


FIG. 3.

Increasing the energy of the molecule and maintaining this type of vibration leads eventually to a complete dissociation of the molecule into A, B and C atoms.

Considerations of this type can, however, only lead to the statement that the probability of decomposition depends upon the shape of the hollow and upon the time the system spends there before escaping. We can say which type of vibration will favour decomposition of a certain kind, but of the problem of the inter-relationship of various kinds of vibration, and of the type of vibration which will be favoured by an increase in total energy of the system such considerations give no information.

3. Let us now transfer our discussion to the particular bond which it is necessary to break in order to bring about decomposition. We will confine our attention to the simple case of a straight chain molecule $A-B-C$ which decomposes into AB and C.

Moreover we will assume that C leaves the molecule in a direction along the line of centres of the three atoms. Eyring and Polanyi⁶ consider that in the reverse

process, the approach of C to AB, such a method of approach involves the least activation energy and it seems reasonable to suppose that in the simple case we are here considering this method of departure of C will lead to the smallest activation energy of decomposition.

Let us consider the potential energy curve produced by the approach of the group AB to the atom C to give a stable molecule ABC. The group AB can exist in various discrete energy levels of vibration the limit of which will be the complete dissociation of AB. The energy curve formed by the approach of AB to C will vary in form according to the vibrational level which AB is occupying. Fig. 2 shows such a series of curves for different states of AB. Curve 1 represents the result when AB is occupying its lowest vibrational level, and curves 2, 3, 4, etc., when AB is occupying successively higher levels. The difference in the value of V_r at $r = \infty$ between these curves is a measure of the energy difference between the various levels of AB.

From the standpoint of this discussion we are chiefly concerned with curves of the type 1 and 4 in Fig. 2 where the latter curve crosses curve 1 at a point above the dissociation energy of curve 1.

In the event of two curves lying in the positions indicated in Fig. 3 there will be the possibility of a radiationless transfer across the energy barrier from region I to region II.

Molecules with a vibrational energy less than E_1 will be unable to undergo transfer. Molecules whose vibrational energy is greater than E_1 but less than E_0 will be able to pass from region I to region II but will still be stable in region II occupying a definite energy level. Molecules with an energy of vibration greater than E_0 possess a certain probability of radiationless transfer across the energy barrier into region II, when decomposition is instantaneous, AB and C moving apart to infinite distance.

Pictorially what happens during such a transfer is that AB drops from the higher vibrational level to a lower one while at the same time AB—C vibration attains a higher vibrational level and a greater amplitude

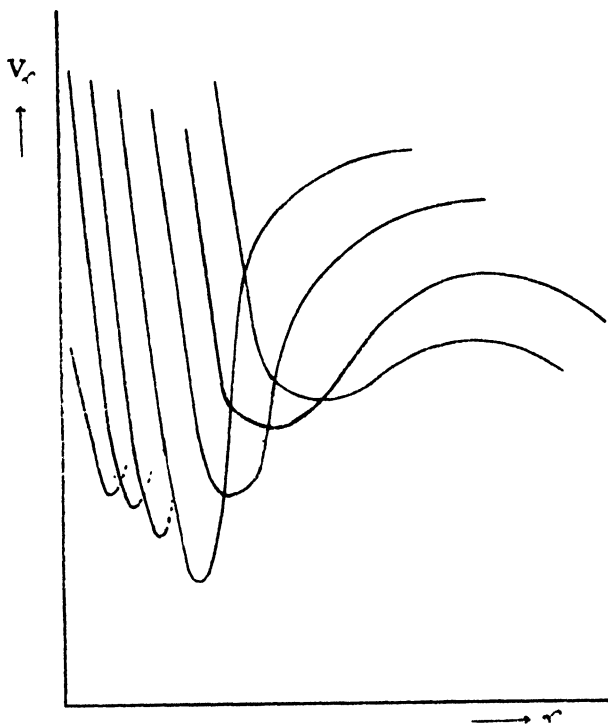


FIG. 4.

of vibration. In the unstable section of region II the vibration of AB—C will be a periodic and dissociation will occur.

We can consider the problem in a similar way from the standpoint of the molecular energy contours, Fig. 1. If we take sections across this diagram at different constant distances of A—B we will have a series of curves for the molecule ABC shown in Fig. 4, representing the energy of the molecule and the type of vibration of AB—C when AB is constant. Again we have curves crossing as in Fig. 3. Here the activation energy E_0 for the decomposition is the height of the energy hump on curve I above the lowest point of the energy hollow, and only those molecules possessing this energy can decompose. Molecules possessing an energy less than E_0 but greater than E_1 will be able to pass from region I to region II,

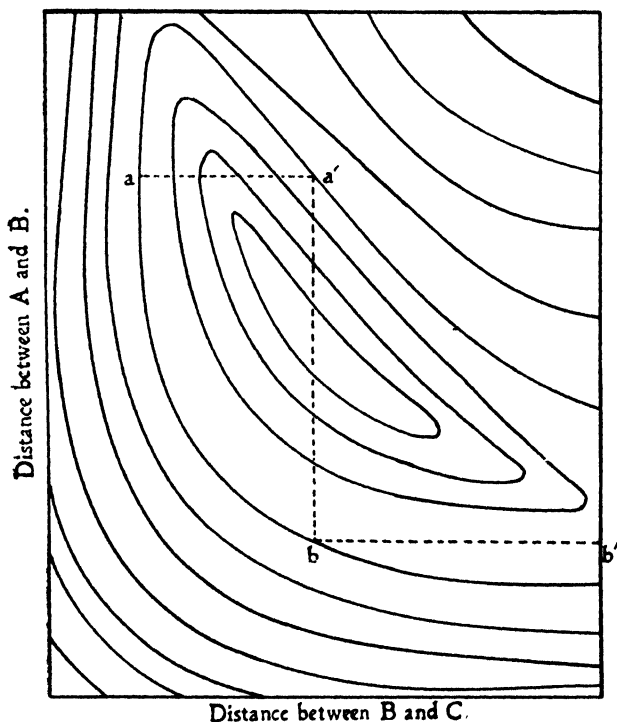


FIG. 5.

I to region II, and change their type of vibration but will not decompose.

Representing these changes on the contour diagram, Fig. 5, if the system is vibrating in a manner indicated by the line aa^1 then (on transition from region I to II), at a^1 the group AB closes up the energy of the system remaining constant indicated by line a^1 to b . The system AB—C now vibrates along bb^1 , and since this is an unstable vibration the mole-

cule decomposes.

The question of unimolecular decomposition viewed in this way is now the probability of escape through the energy barrier.

The probability of a particle passing through an energy wall at a single approach is approximately equal to

$$\exp \left\{ - \left(\frac{4\pi}{h} \right) \int_{r=x_1}^{r=x_2} [2m(V-W)]^{\frac{1}{2}} dr \right\},$$

m being the mass of the particle and x_1 and x_2 being those values of r at which $(V - W)$ vanishes.

Here we are dealing with a function of the type shown in Fig. 3. Insufficient data make it impossible to construct such curves for any

particular molecule, but it has been shown by Bourgin⁴ that escape through such a barrier leads to an equation of the Arrhenius type.

The energy barrier now need not be of such a breadth that the contribution from a non-classical escape becomes negligible. It would appear probable from a qualitative consideration that the more complex the molecule the greater will be the chance that two curves of the type 1 and 4 in Fig. 3 will overlap so as to produce a very thin energy barrier, and we should expect that very approximately, for complex molecules the value of A in equation $k = Ae^{-E/RT}$ to be greater than in the case of simpler molecules. This of course will only be very approximate since the positions of the energy curves will depend upon the coulombic and resonance energies of the particular groups in the molecule in question.

We have tried in this discussion to "bring the rest of the molecule into the picture" and show how the probability of decomposition may depend upon the energy state of the rest of the molecule.

Summary.

The unimolecular decomposition is discussed from the standpoint of non-classical escape through an energy barrier.

The nature of the energy barrier is shown to depend upon the energy of the rest of the molecule.

Manchester University.

STUDIES IN OPTICAL ACTIVITY.

PART I. A CONTRIBUTION TO VALENCE THEORY.

BY CHRISTOPHER HOLLIS JOHNSON.

Received 29th September, 1932.

Broadly speaking, molecules are either aggregates of atoms bound by various kinds of electron bonds, or aggregates of ions. The application of the wave mechanics to problems of molecular structure has resulted in a clearer understanding of the nature of valence forces. The energy of a covalent bond, the electron pair of G. N. Lewis, is composed largely of the exchange energy of the two electrons, whereas the strength of an ionic bond is measured by the potential energy arising from the electrostatic attraction of oppositely charged ions and the repulsion due to their interpenetration. The mutual deformation of ions is no longer considered an important factor in determining molecular structure. It is, however, probable that an accurate expression of the wave function denoting a covalent bond will contain ionic terms, and *vice versa*, so that the specification of a particular bond as of one type or the other depends upon the relative magnitude of the integrals involved.¹ In the majority of cases, differentiation between the two extremes is a practical possibility, and in consequence Pauling has been able to formulate tables of ionic radii for use in constructing ionic compounds and of covalent

¹ Linus Pauling, *J.A.C.S.*, **54**, 3570, 1932.

atomic radii for covalent compounds. The distinction between the terms *ionic* and *covalent* can be illustrated by reference to that interesting class of substances known collectively as *co-ordination compounds*. The process of co-ordination involves the clustering of negatively charged ions or neutral molecules around a small highly charged positive ion. The compound so formed possesses a characteristic set of physical and chemical properties. In cases where the bonds are ionic, the component ions seem to retain their identities except in so far as they cease to function independently. A good example is the ferrifluoride ion, FeF_6^{---} . In other cases, such as $\text{Fe}(\text{CN})_6^{---}$ and $\text{Fe}(\text{CN})_6^{----}$, the units are cemented by electron bonds, or covalently.

A comprehensive theory of co-ordination valency has recently been presented by Linus Pauling,² which enables a forecast to be made of the possible co-ordination numbers, spatial orientations and relative strengths of bonds, provided the ground state of the central positive ion is specified. In order to clarify the subsequent argument, it is necessary to give here a brief, non-mathematical account of the notions underlying Pauling's treatment.

As is well known, atoms are built up of electrons, each of which possesses a unique set of quantum numbers. An electron shell of total quantum number n consists of sub-groups characterised by the quantum number $= l, 1, 2, \dots (n - 1)$, and called respectively, s, p, d, \dots sub-groups. The energy levels associated with a particular total quantum number cannot contain more than two s electrons, six p electrons, or ten d electrons. A chemical bond usually comprises a pair of electrons with oppositely directed spins, and the number and type of bonds formed by an atom depends upon the nature of the electron eigenfunctions available. Normal atoms of elements standing between hydrogen and argon in the Periodic Table possess only s or p electrons. In forming bonds the separate s and p eigenfunctions (Pauling uses the term "eigenfunction" in this way) may either act independently and characteristically, or, when the bond energy happens to be greater than the difference in energy between the s and p levels, may be combined mathematically to give new wave functions which result in stronger bonds having a specific spatial orientation. Combination of one s and three p eigenfunctions gives rise to four equivalent strong bonds directed towards the corners of a regular tetrahedron. This is the fundamental fact underlying the chemistry and stereochemistry of carbon.

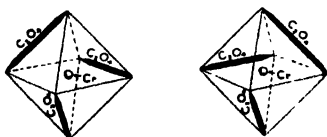
To turn now to the special problem of co-ordination compounds, it is evident that the situation is complicated by the presence of d electrons as well as s and p electrons. For a so-called transitional series of elements arises from the progressive filling of a d sub-group, and the formation of co-ordination compounds is a characteristic property. The first series is the most important and contains the ten elements: Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, and Zn.

For the purpose of this discussion the following result of Pauling's calculations is of paramount importance. When there are available for bond formation two d eigenfunctions these may unite with one s and three p eigenfunctions to give new ones which generate stronger bonds than any of the original eigenfunctions. In this case, the result of combination is six strong, equivalent bonds directed towards the corners of a regular octahedron. An octahedral symmetry for compounds of

² *J.A.C.S.*, **53**, 1367, 1931; **54**, 988, 1932.

co-ordination number, 6, was inferred long ago by Werner from his successful demonstration of optical isomerism in certain of them. Thus, the complex ion $\text{Cr}(\text{C}_2\text{O}_4)_3^{3-}$, was resolved by him, and presumably the structures of the isomeric ions are represented in Fig. 1.

Since that time it has been tacitly assumed that any compound of this sort is capable of resolution into optical isomers given favourable experimental conditions. The purpose of this paper is to call attention to facts which strongly suggest that this is not the case, and to connect the existence or non-existence of optical isomerism with the valence characteristics of the co-ordination compound. Not only is an interesting light thrown upon the phenomenon of optical activity, but in addition a new criterion is provided for distinguishing different types of bonds.



OPTICAL ISOMERS

FIG. 1.

The Magnetic Criterion of Valence.²

The justification of Pauling's valence theory is found in Bose³ and Stoner's⁴ interpretation of the data on magnetic susceptibilities. The theory will doubtless become clearer by application to some specific cases. Several transitional elements give rise to stable ions of the type M^{+++} which co-ordinate with oxalate ions to form trioxalate complexes, $M(\text{C}_2\text{O}_4)_3^{3-}$. The potassium salts of a number of these have been prepared in this laboratory. Mr. A. Mead, B.Sc., prepared and analysed the cobaltioxalate, and Mr. F. E. Smith the corresponding compound of aluminium. The magnetic data at present obtained are summarised in Table I.

All the measurements were kindly made for me by Dr. W. Sucksmith of the Physics Department, to whom I am greatly indebted.

χ_{291° and χ_{90° refer, respectively, to the gram-molecular susceptibilities of the crystalline salts measured at room temperature and at the boiling point of liquid oxygen. The magnetic moments $\mu_{\text{obs}} = 2.83\sqrt{\chi_T(T + \Delta)}$; $\mu_{\text{calc}} = \mu_B = 2\sqrt{S(S + 1)}$. $S = \sum s$, where $s = \frac{1}{2}$ for each unpaired electron. Corrections have been applied for the diamagnetic contributions of the potassium ions and the water molecules. The small values of the Curie Constant Δ might have been anticipated from the steric effect of the oxalate groups which must cause a considerable separation of the paramagnetic metal ions.

The close correspondence between μ_{obs} and μ_B justifies a graphical representation of the states of the central metal ions. These are shown in Fig. 2. The square "boxes" denote single electron positional eigenfunctions, and the arrows stand for electrons. No distinction is drawn between individual boxes in respect of orbital moment because the magnetic data prove that the orbital moment of the electrons is suppressed. In all cases the 1s, 2s, 2p, 3s, and 3p levels are complete.

It is immediately evident from Fig. 2 that the states of Cr and Co satisfy Pauling's criterion for the existence of electron pair bonds. Each

³ *Z. Physik*, **43**, 864, 1927.

⁴ *Phil. Mag.*, **8**, 250, 1929.

TABLE I.—MAGNETIC SUSCEPTIBILITIES.

Compound (Crystalline).	χ_{291° ($\times 10^4$).	χ_{90° ($\times 10^4$).	Δ .	$\mu_{\text{obs.}}$ (Bohr Magnetons).	$\mu_{\text{calc.}}$ (Bohr Mag- netons).	Number of Unpaired Electrons in Molecule.
$\text{K}_3\text{Cr}(\text{C}_2\text{O}_4)_3 \cdot 3\text{H}_2\text{O}$	59.5	186.3	4°	3.75	3.88	3
$\text{K}_3\text{Mn}(\text{C}_2\text{O}_4)_3 \cdot 3\text{H}_2\text{O}$	97.7	284.5	14°	4.88	4.90	4
$\text{K}_3\text{Fe}(\text{C}_2\text{O}_4)_3 \cdot 3\text{H}_2\text{O}$	141.3	458.0	0°	5.75	5.91	5
$\text{K}_3\text{Co}(\text{C}_2\text{O}_4)_3 \cdot 3\frac{1}{2}\text{H}_2\text{O}$	—	—	—	diamagnetic	—	0
$\text{K}_3\text{Co}(\text{C}_2\text{O}_4)_3 \cdot 1\frac{1}{2}\text{H}_2\text{O}$ (dextro-rotatory)	—	—	—	"	—	0
(Strychnine) $_2\text{Co}(\text{C}_2\text{O}_4)_3 \cdot 9\text{H}_2\text{O}$ (laevorotatory)	—	—	—	"	—	0
$\text{K}_3\text{Al}(\text{C}_2\text{O}_4)_3 \cdot 3\text{H}_2\text{O}$	—	—	—	diamagnetic	—	0

has two d eigenfunctions available for combination with those characteristic of the $4s$ and $4p$ levels. But the states of Mn and Fe do not satisfy the criterion.

According to the rules deduced from atomic spectra, the normal state of an ion is that possessing the maximum multiplicity, *i.e.*, the largest number of unpaired electrons. It is therefore obvious that reference to the magnetic data cannot decide between the ionic and the electron bond structure for $\text{Cr}(\text{C}_2\text{O}_4)_3$ ---. Chromic ion has only three d electrons to accommodate, so that two of the d boxes are necessarily unoccupied. In this case bond formation can occur without alteration

	3d	4s	4p
Cr IN $\text{Cr}(\text{C}_2\text{O}_4)_3$ ---			
Mn IN $\text{Mn}(\text{C}_2\text{O}_4)_3$ ---			
Fe IN $\text{Fe}(\text{C}_2\text{O}_4)_3$ ---			
Co IN $\text{Co}(\text{C}_2\text{O}_4)_3$ ---			
Co IN $\text{Co}^{III}\text{ALUM}$			

FIG. 2.

of the total spin moment. The gram-molecular magnetic susceptibility of

$\text{K}_3\text{Cr}(\text{C}_2\text{O}_4)_3$ is almost identical with that of CrCl_3 . The two alternative structures are represented in Fig. 3.

On the other hand, the diamagnetism of

$\text{Co}(\text{C}_2\text{O}_4)_3$ ---

indicates that all the unpaired electrons of cobaltic ion have become paired in the process of bond formation. Contrast the condition of cobaltic ion in cobaltic alum in which it is paramagnetic to the extent of 5.2 Bohr magnetons. This is shown in Fig. 2. The magnetic data definitely point to ionic structures for both $\text{Mn}(\text{C}_2\text{O}_4)_3$ --- and $\text{Fe}(\text{C}_2\text{O}_4)_3$ ---, similar to that illustrated in Fig. 3. It is noteworthy that Welo⁵ has

⁵ *Phil. Mag.*, 6, 481, 1928.

measured the magnetic susceptibilities of a large number of complex salts of ferric ion, and his results suggest ionic structures in every case except that of ferricyanide.

The bearing of these facts upon the phenomenon of optical activity can be briefly stated. The trioxalate complexes of chromium and cobalt are known to exhibit optical isomerism. A comprehensive study of the cobalt complex will appear in Part III. of this series. On the other hand, all attempts made in this laboratory to effect the resolution of $K_3Mn(C_2O_4)_3$ and $K_3Fe(C_2O_4)_3$ have been unsuccessful. It is difficult to resist the conclusion that resolution into optical isomers is only practicable when electron bonds unite the components of a molecular ion. If such is the case, then $Cr(C_2O_4)_3$ cannot possess an ionic structure. Considerable further evidence in support of this conclusion will be presented in a subsequent passage. Since the argument rests upon an experimental study of the iron and manganese salts, a reasonably full description of this phase of the work is necessary.

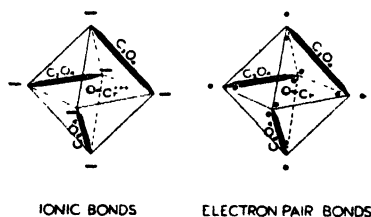


FIG. 3.

Attempts to Resolve the Trioxalates of Fe^{+++} , Mn^{+++} and Al^{+++} .

$K_3Fe(C_2O_4)_3 \cdot 3H_2O$.—W. Thomas⁶ was unable to resolve the salt with strychnine, but claimed to have succeeded with the optically active base, α -phenyl ethylamine.

During the past year several attempts have been made here to resolve the compound with strychnine simply because the reasons tendered by Thomas to explain his failure with this base appeared to be unsatisfactory. Thomas states that the green aqueous solution of strychnine ferrioxalate is unstable, and that even in the dark it becomes colourless in twenty-four hours consequent upon the precipitation of di-strychnine ferro-oxalate. Presumably this precipitate was analysed. Taking into consideration the known properties of the ferrioxalate ion, these results are really extraordinary. For the ion is remarkably stable in the absence of blue light. According to Abegg,⁷ an aqueous solution of potassium ferrioxalate can be boiled for three days in the dark without appreciable decomposition. Moreover, $Co(C_2O_4)_3^{---}$ and $Mn(C_2O_4)_3^{---}$, although decomposing rapidly at temperatures in the neighbourhood of $100^\circ C.$, give rise to crystalline strychnine salts which are quite stable at room temperatures.

My experimental observations sharply contradict those of Thomas. An aqueous solution of strychnine ferrioxalate is greenish yellow and remains so for days in the dark, indeed until all the water has evaporated, whilst slowly depositing greenish yellow crystals. That these crystals are the strychnine salt of the ferrioxalate and not of the ferro-oxalate can be convincingly demonstrated without resort to analysis. Thus, a few of them are crushed and added to 5 c.c. of potassium iodide solution. The precipitated strychnine iodide is removed by filtration, and the clear

⁶ *J.C.S.*, 119, 1140, 1921.

⁷ *Handbuch Anorg. Chem.*, 4, 381, 1930.

yellowish green filtrate left to evaporate in a dark cupboard. After a day or two, brilliant "emerald-green" crystals of the not very soluble potassium ferrioxalate appear, which cannot possibly be mistaken for yellow ferrous oxalate. It may be that the usual description of these crystals as "emerald-green" is partly responsible for Thomas's error, for it is certainly misleading. Crystals of potassium ferrioxalate are often large and lustrous, but definitely yellowish green and not emerald green. When finely precipitated or powdered they are canary yellow, as are the barium salt and the derivatives of several organic bases.

The methods used in attempts to resolve the compound were modelled on those developed successfully in the work on cobaltioxalate (Part III.). Only lævorotatory solutions were ever obtained; the optical activity did not change on standing, and was entirely lost when the strychnine was removed. There is no doubt that the salt cannot be resolved with strychnine. Unsuccessful experiments with strychnine, cinchonine, quinine and morphine have been reported by Jaeger.⁸

Thomas claims to have resolved the substance by means of α -phenylethylamine. His method was to mix aqueous solutions of the hydrochloride of the active base and potassium ferrioxalate in equivalent proportions, and allow the mixture to evaporate slowly in the dark. If there exists a difference of solubility between the *d* and *l* ferrioxalates of the active base, the precipitation of the least soluble component followed by the rapid racemisation of the more soluble component in solution, further precipitation and evaporation, will eventually result in the complete transformation of the racemic ferrioxalate into one or other of the optical isomers. Under favourable circumstances the precipitated material will consist largely of the lævo or dextrorotatory ferrioxalate of the active base. Thomas states that an actual experiment with lævorotatory α -phenylethylamine, gave first an inactive crop of crystals and then a series of lævorotatory crops which when dissolved in water lost their activity in the course of an hour. Similar results in an opposite sense were obtained with the dextrorotatory base.

These experiments have been carefully repeated here. Dextro and lævorotatory α -phenylethylamine were prepared from the racemic base by the method of Lovén⁹ and dissolved in equivalent quantities of 2*N* hydrochloric acid. The procedure outlined above was followed. Successive crops of well-formed yellow crystals of α -phenylethylamine ferrioxalate were obtained. These were quickly dissolved in just sufficient ice-cold water to fill a 25 cm. polarimeter tube which was examined in the polarimeter within ten minutes of making up the solution. The yellow and green lines of the mercury arc served as light sources. The ferrioxalate ion is without parallel amongst the coloured trioxalates in respect of its high degree of transparency throughout almost the entire visible region. This property is of great assistance in making polarimetric observations. The crops of crystals were invariably active although the first consisted chiefly of potassium racemate. The sign of rotation was always the same as that of the base used, and was never observed to change with time. A curious feature of the work of Thomas is his inability to detect the activity of the bases. According to him, the rotation of an aqueous solution gradually falls to zero, whereas my values range between $\pm 0.04^\circ$ and $\pm 0.35^\circ$ depending on the concentration of

⁸ Jaeger, *Rec. Trav. Chim.*, **38**, 242, 1919.

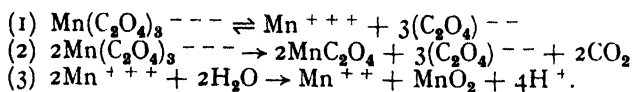
⁹ *J. Prakt. Chem.*, **72**, 307, 1905.

the solution. These are of the same order of magnitude as those quoted by Thomas and attributed to the complex ion.

The method recommended by Thomas for converting α -phenylethylamine ferrioxalate to the potassium salt by precipitation of the barium salt and subsequent removal of the barium by addition of potassium sulphate, proved unsatisfactory. Either the barium salt adsorbed traces of the active base or, possibly, Ba-base-ferrioxalate was occluded in the precipitate, because the final solution (which should have contained only potassium ferrioxalate and the excess of potassium sulphate) sometimes showed slight permanent activity to the extent of 0.01° or 0.02° in a 25 cm. tube, dextro or lævorotatory according to the sign of the base used. Moreover, the slow precipitation of barium sulphate frequently caused cloudiness in the polarimeter tube, thereby making rapid measurements impossible. This difficulty was overcome by substituting potassium oxalate for potassium sulphate.

These experiments, therefore, do not confirm those of Thomas. Further attempts to effect resolution were made as follows. A gram of potassium ferrioxalate was dissolved in 2 c.c. of hot water, and to this was added about 4 c.c. of a solution containing an equivalent amount of the hydrochloride of the dextro or lævorotatory base. The mixture was chilled in an ice bath and stirred vigorously. After two or three minutes a considerable precipitate formed which was quickly separated by filtration and dried by suction. The filtrate was diluted with about 20 c.c. of ice-cold water, placed in a suitable polarimeter tube, and immediately examined. The residue was afterwards extracted with ice-cold water and successive extracts examined in the polarimeter. No evidence of autoracemisation was obtained, and it was proved conclusively that the measured activities of these solutions were due entirely to the optically active base.

$K_3Mn(C_2O_4)_3 \cdot 3H_2O$.—The salt was prepared by the method of Kehrman,¹⁰ and purified by precipitation with alcohol from concentrated aqueous solution. Of all compounds of this class, it is the most difficult to investigate on account of instability with respect to several types of decomposition, *viz.*,



Reaction (1) is common to all members of the trioxalate series. Reaction (2) takes place fairly quickly in aqueous solution at room temperatures, even in the dark. In daylight the precipitation of manganous oxalate is extremely rapid. On dilution with water, the deep cherry red colour characteristic of $Mn(C_2O_4)_3^{---}$ passes through various shades of red and brown and, ultimately, manganese dioxide is precipitated, (3). From these facts it is obvious that concentrated solutions must be used in attempts to resolve the salt. The experiments were performed as quickly as possible, in a dim light and often at ice-temperature. The magnificent colour of the $Mn(C_2O_4)_3^{---}$ ion is a helpful indication of its continued existence under various circumstances, but its great absorbing power is a severe obstacle to polarimetric work. Consequently narrow glass cells of thickness 0.25 and 1.0 cm. have been used in place of polarimeter tubes. No previous attempts to resolve this compound

are known to the writer. Strychnine appears to be the patron-base of the trioxalates and was therefore selected for the first experiments.

One gram of the salt was dissolved in 5 c.c. of water to which was then added, with stirring, about 100 c.c. of a saturated solution of neutral strychnine sulphate containing an equivalent amount of the base. The pink crystalline precipitate of the strychnine salt was filtered off, and part of the filtrate examined in the polarimeter. The remainder of the filtrate was left to cool in an ice-bath. The residue was extracted with ice-cold water (or, alternatively, ice-cold aqueous potassium oxalate to minimise the decomposition of the complex ion) and the successive extracts were immediately examined for rotatory power. Meanwhile the original filtrate in the ice-bath had deposited a further crop of crystals. These were quickly dissolved in ice-cold water and taken to the polarimeter. Several experiments were conducted in this fashion but no positive indications of resolution were obtained. The small, permanent, lævorotations (about 0.05°) were certainly due to strychnine. Negative results were also recorded with cinchonine. The manganioxalate of α -phenyl ethylamine proved to be exceedingly soluble in water and no precipitation could be achieved even in the manner described in the case of the iron compound. Attempts to evaporate aqueous solutions containing active α -phenyl ethylamine hydrochloride and potassium manganioxalate were frustrated by the rapid decomposition of the complex ion.

Further efforts will be made, but even now it is tolerably certain that the compound cannot be resolved with strychnine.

$\text{K}_3\text{Al}(\text{C}_2\text{O}_4)_3 \cdot 3\text{H}_2\text{O}$ —This salt is said to have been resolved into optically active components by Wahl¹¹ in 1927. Therefore, the complex must be cemented by electron bonds. This is interesting because Al^{+++} has a neon-like structure and the bonds could only arise by combination of $3s$, $3p^3$, and $3d^2$ eigenfunctions. But the rather large separation of the s and d , and p and d levels makes this combination unlikely. The point cannot be decided from magnetic measurements since the substance is diamagnetic (Table I.). The salt is colourless and very soluble, and therefore ideal for polarimetric investigations. The method of resolution described by Wahl is extremely simple, and consists merely of fractional extraction of the tristrychnine derivative, $\text{Str}_3\text{Al}(\text{C}_2\text{O}_4)_3$. The residue remaining after three or four extractions is said to be dextro-rotatory.

My attempts to confirm this statement have been fruitless. Only lævorotatory residues (and extracts) were obtained, of which the activities did not change with time whereas Wahl reported a slow racemisation. Removal of the strychnine caused the disappearance of rotatory power in every case. It appears that Wahl took no account of the activity of the base. Further attempts were made with strychnine, cinchonine and α -phenyl ethylamine by application of the methods already described in the sections dealing with ferri and manganioxalates. All the results were negative. Finally, the slow evaporation of a solution of the tristrychnine salt was tried. As previously explained, this is a powerful means of effecting resolution under favourable circumstances. The essential conditions are as follows: the complex ion must be stable in solution; there must be an appreciable difference of solubility between the dextro and lævorotatory derivatives of the active base; and race-

¹¹ *Ber.*, 60, 399, 1927.

misation must occur in solution. According to the findings of Wahl, every one of these requirements is fulfilled. In addition, the solutions possess the unique advantage of being perfectly transparent to visible light. Therefore an aqueous solution of $\text{Stry}_3\text{Al}(\text{C}_2\text{O}_4)_3$ was allowed to evaporate slowly over a period of ten days. By this time about half the water had disappeared and two or three grams of crystals had deposited. These were separated, and at once converted to the potassium compound by addition of just sufficient ice-cold aqueous potassium iodide to fill a 30 cm. polarimeter tube. After filtering off the strychnine iodide, the entire solution was examined in the polarimeter and found to be optically inactive.

Thus, Wahl's result has not been confirmed. The complex trioxalate of aluminium takes its place in the group of ionic complexes along with the corresponding salts of iron and manganese with which it is isomorphous. If this is a guide to the condition of Al^{+++} in its complex ions, then AlF_6^{---} must be placed in the same category.

Optical Activity as a Criterion of Valence Type.

Much additional evidence is to be found in the literature in support of the idea that the phenomenon of optical isomerism in complex salts is conditioned by valency characteristics.

Apart from the trioxalate complexes already mentioned, the only others so far resolved are those of the other metals in Group VIII., namely $\text{Rh}(\text{C}_2\text{O}_4)_3^{---}$ and $\text{Ir}(\text{C}_2\text{O}_4)_3^{---}$, the former by Werner¹² and Jaeger¹³ and the latter by Jaeger¹⁴ and Delépine¹⁵. No magnetic measurements have been made of these ions, but they are certain to be diamagnetic. The triethylenediamine salts of Rh^{+++} are diamagnetic, and so are some compounds of Ir^{+++} , having a co-ordination number 6¹⁶. The behaviour of these complex ions is thus precisely similar to that of the corresponding derivative of cobalt. Analogous to the trioxalate complexes are the trimalonates, for malonic acid, $\text{COOH} \cdot \text{CH}_2 \cdot \text{COOH}$, is the next higher homologue of oxalic acid. The chromimalonate, $\text{Cr}(\text{C}_3\text{H}_2\text{O}_4)^{---}$, and the rhodimalonate, $\text{Rh}(\text{C}_3\text{H}_2\text{O}_4)^{---}$, have been resolved by Jaeger,¹⁷ but he was unable to resolve the ferrimalonate. It is significant that in the latter case he tried the bases strychnine, brucine, and cinchonine, and attempted to minimise the possible occurrence of autoracemisation by working with solutions of aqueous acetone. A solution of the cobaltimalonate is reported to be excessively unstable even at ordinary temperatures and in the absence of light. For this reason, Thomas⁶ was unable to obtain the optical isomers. However, unless the compound turns out to be paramagnetic, which is improbable since it is dark green like the trioxalate salt, it ought to be possible to demonstrate optical isomerism. This point is under investigation.

Another important series of co-ordination compounds possessing octahedral symmetry are the triethylenediamine salts of transitional elements. Three molecules of ethylenediamine, $\text{NH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NH}_2$, are each attached at two points to the central metal ion, M^{+++} . Werner resolved salts of $\text{Co}(\text{en})_3^{+++}$, $\text{Rh}(\text{en})_3^{+++}$, and $\text{Cr}(\text{en})_3^{+++}$, and some years later Jaeger¹⁸ extended the work and measured their rotation dispersion. The first two compounds are diamagnetic,²⁰ and the chromic

¹² *Ber.*, **47**, 1954, 1914.

¹³ *Loc. cit.*, p. 256.

¹⁴ *Loc. cit.*, p. 270.

¹⁵ *Bull. Soc. Chim.*, **21**, 157, 1917.

¹⁶ Bose, *Z. Physik*, **65**, 677, 1930.

¹⁷ *Loc. cit.*, p. 285.

¹⁸ *Loc. cit.*, p. 180.

compound is paramagnetic to the same extent as $\text{Cr}(\text{C}_2\text{O}_4)_3^{---}$. Thus a complete parallelism exists between the behaviour of the ethylenediamine and the oxalate complexes. It is not surprising to find that the triethylenediamine complex of Fe^{+++} is extremely unstable.

The triethylenediamine salts of Ni^{++} , Cu^{++} , Zn^{++} , and Cd^{++} have been prepared, and efforts made to resolve them but without success.¹⁹ All are of the ion-dipole type and therefore unresolvable according to the hypothesis developed in this paper. The ion-dipole structure is clearly indicated for $\text{Ni}(\text{en})_3^{++}$ since the paramagnetism²⁰ corresponds to the presence of two unpaired electrons in the d shell. Therefore none of the d eigenfunctions are available for bond formation.

This catalogue is by no means exhaustive. The most recent addition to the list of optically isomeric compounds is a carbon-free complex ion of Rh^{+++} co-ordinated with two molecules of sulphamide and two of water. It was prepared and resolved by Mann.²¹ A *cis* derivative necessarily involves (d^2sp^3) eigenfunctions, and the water molecules are therefore bound to the central ion by electron pair bonds, a rather unusual circumstance. The corresponding *trans* structure will likewise be diamagnetic, but an alternative *trans* structure can be imagined generated from (dsp^2) eigenfunctions in which the water molecules are attached by ion-dipole bonds. In the latter event, the compound will be paramagnetic to the extent of about 2.8 Bohr magnetons. If a *trans* compound can be prepared, the determination of its magnetic susceptibility is desirable from this point of view.

Discussion.

It has been taken for granted that complex ions of the type $\text{M}(\text{C}_2\text{O}_4)_3^{---}$ possess similar configurations and the same co-ordination number, 6. But the only facts which are at present established are the exact correspondence of the molecular formulæ of the potassium trioxalates of Al^{+++} , V^{+++} ,²² Cr^{+++} , Mn^{+++} , and Fe^{+++} , and the isomorphism of their crystals, all of which occur in the monoclinic system with three molecules of water per mol. of salt. The corresponding derivatives of Co^{+++} , Rh^{+++} and Ir^{+++} are said to be triclinic and to contain respectively, $3\frac{1}{2}$, $4\frac{1}{2}$, and $4\frac{1}{2}$ molecules of water. Dr. S. H. Piper, of the Physics Department, has kindly undertaken an X-ray examination of the crystals in the hope of gaining further information.

The simplest explanation of the failure to effect resolution of complex ions in which configurational dissymmetry is assumed to exist, is to postulate a rapid rate of racemisation of the optical isomers. There is reason to think that in those cases where resolution has been achieved, partial ionisation of the complex is an essential step in the racemisation process. Thomas and Fraser²³ found that an aqueous solution of $\text{K}_3\text{Cr}(\text{C}_2\text{O}_4)_3$ possessed a larger concentration of free oxalate ions and a higher rate of autoracemisation than $\text{K}_3\text{Co}(\text{C}_2\text{O}_4)_3$ under comparable conditions. But although $\text{K}_3\text{Fe}(\text{C}_2\text{O}_4)_3$ is in equilibrium with a somewhat smaller concentration of oxalate ion than the chromic salt, this cannot be urged as a conclusive argument against the assumption that ferrioxalate ion is unresolvable because of its fast rate of racemisation, since the ferric complex differs from the other two in valency character.

¹⁹ *Loc. cit.*, p. 237.

²¹ *Nature*, **130**, 368, 1932.

²² *J.C.S.*, **123**, 2973, 1923.

²⁰ Rosenbohm, *Z. physik. Chem.*, **93**, 693, 1919.

²³ *Under investigation here.*

There exists no positive evidence of autoracemisation in the crystalline state, and for this reason the study of rotatory dispersion in a single crystal of strychnine- (or α -phenyl ethylamine-) ferrioxalate would be of interest. The practical difficulties may be considerable and the results must necessarily be complicated by the effects of birefringence and the presence of an optically active base.

Alternatively, the ionic type of binding may be unfavourable to the production of optical activity. Werner Kuhn²⁴ has deduced the essential features of an optically active molecule. These comprise at least one pair of coupled vibrators, separated by a finite distance, of which the axes of vibration are not parallel. The optimum conditions are realised when the components of the vibrating electric moment are equal in magnitude and at right angles to one another. Unfortunately, very little is known about the factors controlling the coupling of individual atomic vibrations, and there exists no information whatever upon the different modes of vibration in the molecules under consideration. As yet, no Raman spectra have been attempted. It is therefore impossible at present even to speculate upon the phenomenon of coupling in relation to bond type. With regard to the spacial distribution of the vibrating electric moments it would be anticipated that the presence of electron bonds (*i.e.*, directed valencies) should promote the development of optical rotatory power.

Another source of conjecture arises from consideration of the electron states of the metal ions in those salts which have resisted attempts to resolve them. The magnetic data indicate that the ferric ion in $\text{Fe}(\text{C}_2\text{O}_4)_3$ --- is in a ${}^6\Sigma$ state. Now Σ states are associated with a spherically symmetrical distribution of electron density, and this condition may be responsible for the non-appearance of optical rotatory power. In other cases, the magnetic data can only be interpreted on the assumption of the more or less complete suppression of orbital moment of the electrons. The magnetic moments are compounded of spin moment only, and in this sense the ground states can be regarded as Σ states.

Throughout this paper attention has been confined to complex ions of which the optical activity, if present, is a property of the ion as a whole and not due to an asymmetry possessed by one or more of the co-ordinated units. But many cases can be cited in which the anion of an optically active acid confers optical activity upon a characteristic absorption band of a coloured metal ion, or, to use Werner Kuhn's phraseology, where *anisotropy* has been induced in the absorption band of the cation by virtue of the *vicinal function* of absorption bands belonging to the optically active anion. The nett result is the appearance of circular dichroism and anomalous rotatory dispersion in the visible region of the spectrum. Two famous examples of this phenomenon are the complex aqueous solutions of "potassium cupric tartrate" and "potassium chromic tartrate," originally studied by Cotton²⁵ and subsequently the subjects of investigation by numerous authors. The latest contribution is that of Werner Kuhn and Szabo,²⁶ whose results suggest that the broad absorption band of "potassium chromic tartrate" (maximum absorption at 5960 Å.) is entirely responsible for the enormous molecular rotatory power in the visible region.

The bearing of this work on the present discussion is that many authors.

²⁴ *Trans. Faraday Soc.*, **26**, 293, 1930.

²⁵ *Ann. Chim. Physique*, **8**, 347, 1896.

²⁶ *Z. physik. Chem.*, **15B**, 59, 1931.

have expressed the opinion that "chemical action" between "an optically active liquid" and a "coloured liquid" (to quote Cotton²⁷) is essential for the manifestation of circular dichroism. Mixing is insufficient. Quite recently Mathieu²⁸ has found that chromic hydroxide dissolves in excess of tartaric acid with the production of a blue-violet solution having a normal rotatory dispersion and no circular dichroism. But, on standing, the solution slowly becomes deep violet and no longer gives a precipitate when treated with ammonium hydroxide. The rotation of the solution is anomalous and the dichroism measurable. The change is attributed to the transformation from heteropolar to homopolar bonds. Obviously the conclusions of these authors are largely speculative since no data have been obtained which could decide the extent of "chemical action" nor determine the type of bonds present. However, it may prove true that covalent bonds must unite a coloured metal ion to an optically active anion if circular dichroism is to appear in the visible spectrum. Dichroism has been detected²⁹ in solutions containing tartrate and the following metal ions: Cr^{+++} , Mn^{++} , Co^{++} , Ni^{++} , Cu^{++} , UO_2^{++} and "Didymium⁺⁺⁺". Some malates and lactates also show the phenomenon. The chromic ion is particularly well suited to the formation of electron bonds, and is actually the only positive ion known to give a dichroic solution with lactic acid. Olmstead's attempts to detect circular dichroism in the presence of Fe^{+++} were unsuccessful. Generally speaking, the addition of a base is needed to bring about solution of the simple tartrates. The resulting solutions doubtless contain a number of distinct chemical compounds, are usually unstable, and give rise to excessively complicated curves of dichroism and rotation-dispersion.

Summary.

It seems that optical isomerism is only observed in co-ordination compounds when the co-ordinated groups are attached to the central ion by covalent bonds. Examples are provided by the trioxalate and triethylenediamine compounds of Cr^{+++} and Co^{+++} . No resolution can be achieved if the components of the molecular ion are united by ionic bonds. Hence a new criterion presents itself for determining the valency characteristics of co-ordination compounds. A review is given of the more important work bearing on the subject, and tentative explanations are suggested of the failure to demonstrate optical isomerism in complex salts of the ionic type.

Particular attention has been devoted to the trioxalates of transitional elements. The resolution into optical isomers of $\text{K}_3\text{Fe}(\text{C}_2\text{O}_4)_3$ and $\text{K}_3\text{Al}(\text{C}_2\text{O}_4)_3$, previously reported by other workers has not been confirmed, and attempts to resolve $\text{K}_3\text{Mn}(\text{C}_2\text{O}_4)_3$ have so far proved fruitless. Therefore the inference is drawn that these three complex ions are stabilised by ionic linkages. The magnetic susceptibilities of the ferri and mangani salts corroborate this view. The magnetic and optical-activity criteria of valence lead to identical conclusions when both can be applied. But the second criterion is able to furnish information in cases where the first is powerless. Thus definite assertions can now be made regarding the types of bonds in Cr^{+++} complexes and $\text{Al}(\text{C}_2\text{O}_4)_3^{---}$ as a result of studies in optical activity.

*Department of Chemistry,
University of Bristol.*

²⁷ *Trans. Faraday Soc.*, **26**, 377, 1930.

²⁸ *C.R.*, **193**, 1079, 1931.

²⁹ Olmstead, *Physic. Rev.*, **35**, 31, 1912; Bruhat, *Ann. Physique*, **3**, 232, and 417, 1915; *ibid.*, **13**, 25, 1920.

ON THE MEASUREMENT OF MECHANICAL PROPERTIES OF BINARY INORGANIC SALT MIXTURES.

BY K. LAYBOURN AND W. M. MADGIN.

Received 4th October, 1932.

In the following study of the mechanical properties of the three binary inorganic salt systems $\text{Pb}(\text{NO}_3)_2/\text{NaNO}_3$, $\text{Pb}(\text{NO}_3)_2/\text{KNO}_3$, and $\text{NaNO}_3/\text{KNO}_3$, it has been found that, in addition to standardised conditions of casting and cooling of specimens, annealing and solvent treatment are of the utmost importance in obtaining consistent results. While Kurnakow and co-workers¹ have measured Brinell hardness and pressure necessary to produce flow in certain binary mixtures of inorganic salts, they do not appear to have considered the possible effects of annealing such specimens. The present work was undertaken both as a study of the conditions necessary for consistent results and as a comparison of the properties of the three systems under review. Both of the binary systems involving $\text{Pb}(\text{NO}_3)_2$ have been shown to be of the simple eutectic type,² while NaNO_3 with KNO_3 forms a continuous series of solid solutions.³

A convenient means of comparing the systems and of examining the effects of solvent treatment is afforded by measurements of transverse breaking strength (the horizontal pull necessary to break a rod casting over two knife edges). Compression strengths also have been determined for the system $\text{NaNO}_3/\text{KNO}_3$, and values have been obtained which show the effects of varying periods of annealing. In addition, Brinell hardness figures have been measured for all three systems, but it should be noted that both transverse breaking tests and compression tests possess certain advantages (discussed later) over determinations of Brinell hardness in the case of inorganic salts.

Joffé and Ewald⁴ and Polanyi⁵ have observed that the tensile strength of rock salt is greater under water than in air, and it seemed reasonable to suppose that atmospheric moisture might have a marked effect on the strengths of the castings used in the present work, since all the nitrates possess a considerable solubility in water. In the experiments now described it has been found necessary to treat all specimens with solvents to remove the effects of previous exposure, and to protect against subsequent attack by atmospheric moisture by coating the specimens with oil.

Experimental.

1. Transverse Breaking Strength.

Apparatus.—This is shown diagrammatically in Fig. 1. The specimen *S* ($\frac{1}{4}$ -inch diam. \times $3\frac{1}{4}$ -inch long) is held loosely in a double collar *C*

¹ *Z. anorg. Chem.*, **74**, 89, 1912; and earlier papers.

² Glass, Laybourn and Madgin, *J. Chem. Soc.*, 874, 1932.

³ Laybourn and Madgin, *J. Chem. Soc.*, 2582, 1932.

⁴ *Z. Physik*, **22**, 286, 1924.

⁵ *Trans. Faraday Soc.*, **24**, 72, 1928.

($1\frac{1}{4}$ inches between collars), the inner surfaces of which are bevelled to ensure point contact only. A brass wire, attached to *C*, passes

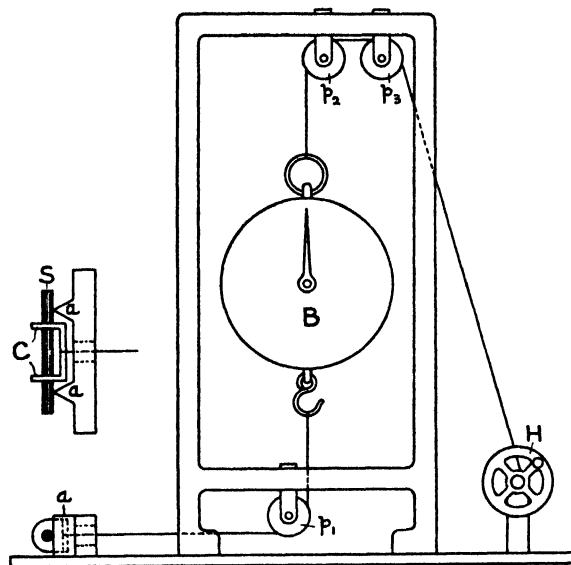


FIG. 1.

centrally through the knife - edges piece *aa* over the pulley *p*₁ to a spring balance *B*, which is in turn attached by a second brass wire, over pulleys *p*₂ and *p*₃, to a screw winding handle *H*. With the handle *H* a steady pull can be transmitted to *C*, and the specimen *S* then breaks in a uniform manner on the knife - edges. These knife - edges are 2 inches apart.

In transverse breaking tests of this kind the specimen does not require to be gripped

as in tensile tests, and, in view of the brittle nature of salt castings, this is an obvious advantage.

Casting of Specimens.—The salts used in these and all other tests described were purified as stated by Glass, Laybourn and Madgin.² The various mixtures used were synthesised by fusing together the appropriate quantities of pure components in hard glass test tubes heated electrically. These melts were poured into gun metal split moulds which contained three separated circular casting holes ($\frac{1}{4}$ -inch \times $3\frac{1}{4}$ inches), each provided with a feed trough to repair "pipes" developed during setting. Cold casting was useless on account of premature setting of the melt with consequent irregular castings and coring. The moulds were therefore heated in an electric furnace packed with sand. It was also necessary to overheat the melts above the freezing-points so that (a) they did not set in the tube during pouring, and (b) extrusion of molten material within the moulds (resulting in winged castings) was avoided. The conditions finally adopted were :

- (1) $\text{KNO}_3/\text{NaNO}_3$ mixtures : Mould 75° below, melt 50° above F.P.
- (2) $\left\{ \begin{array}{l} \text{Pb}(\text{NO}_3)_2/\text{NaNO}_3 \text{ and} \\ \text{Pb}(\text{NO}_3)_2/\text{KNO}_3 \text{ mixtures} \end{array} \right\}$ Mould 100° below, melt 25° above F.P. of melt.

Pure sodium and potassium nitrates and the mixture of lowest freezing-point in each system were found to develop large "pipes" in the centre when setting, and feeding with melt was very necessary in these cases. Castings were kept in desiccators pending testing.

Annealing and Solvent Treatment.—Widely varying results obtained with earlier castings suggested that annealing would be desirable, and accordingly all rods were finally heated in close fitting glass tubes (to prevent distortion) for six days at temperatures 10° below the

minimum freezing-point in the appropriate systems. The freezing-point data are given by Briscoe and Madgin⁶ and Glass, Laybourn and Madgin.² A specially constructed electric furnace was used to give uniform heating during annealing, and specimens were finally cooled off in the furnace. This annealing, resulted in greater consistency, but the values were still conditioned by the time of exposure in the ordinary atmosphere between removal from the desiccator and testing. The effect of varying exposure to the atmosphere is shown by the following figures, obtained for seven annealed specimens of the same composition (45 per cent. KNO_3 , 55 per

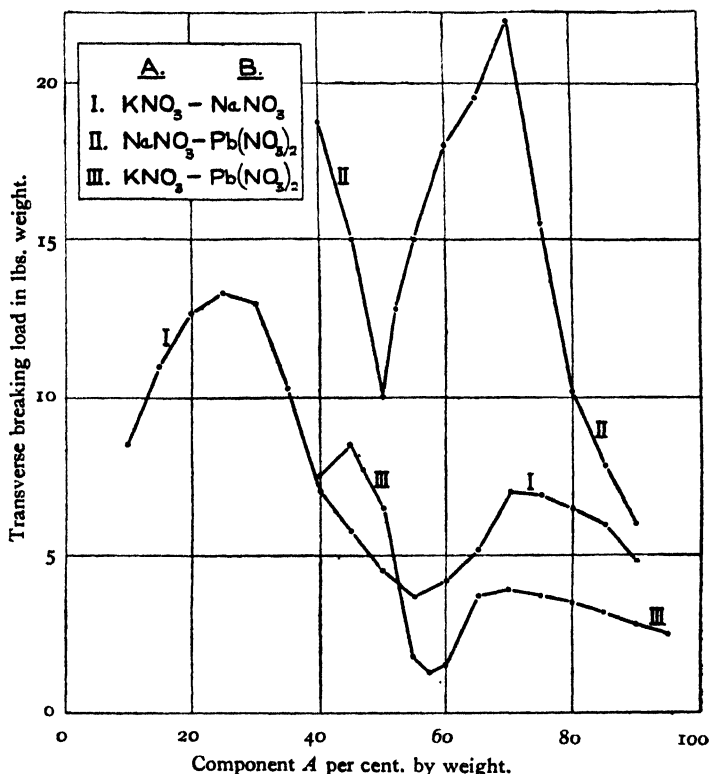


FIG. 2.—Transverse breaking strength/composition diagrams for the systems $\text{NaNO}_3/\text{KNO}_3$, $\text{Pb}(\text{NO}_3)_2/\text{NaNO}_3$ and $\text{Pb}(\text{NO}_3)_2/\text{KNO}_3$.

cent. NaNO_3). The specimens were all removed from the dessicator simultaneously, and tested consecutively in the order shown :

Time of exposure (mins.)	0	5	10	15	20	25	30
Breaking strength (lbs.)	6	8	9.5	11.5	12.5	14.5	15

Believing these wide variations to be due to the effects of moisture, the following method of solvent treatment was adopted. Each specimen was dipped in distilled water to remove the effects of atmospheric moisture on the surface. The specimen was then dipped in alcohol and ether successively to remove the water, and, when dry, it was dipped in medicinal paraffin oil ; this gave a protective coating from moisture, and

adhered to the specimen during testing. Tests on specimens thus treated gave consistent and reproducible results, although the values were considerably lower than those for untreated specimens. The same degree of reproducibility was not attained, however, in the case of castings which had been treated with solvents, but had not been annealed, and it is therefore evident that the conditions necessary for really satisfactory results are annealing, solvent treatment and surface protection.

TABLE I.—EXPERIMENTAL DATA FOR TRANSVERSE BREAKING STRENGTHS (T.B.S.).

(Compositions expressed as weight per cent. of the component stated.)

Series I.— NaNO_3 with KNO_3 .																			
% KNO_3	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90		
T.B.S. in lbs.		8.5	11	12.7	13.3	13	10.3	7	5.8	4.5	3.7	4.2	5.2	7	6.9	6.5	6	4.8	
Series II.— $\text{Pb}(\text{NO}_3)_2$ with NaNO_3 .																			
% NaNO_3		40	45	47	50	55	57.7	60	65	70	75	80	85	90	95				
T.B.S. in lbs.		7.5	8.5	7.7	6.5	1.75	1.25	1.5	3.7	3.9	3.7	3.5	3.2	2.8	2.5				
Series III.— $\text{Pb}(\text{NO}_3)_2$ with KNO_3 .																			
% KNO_3			40	45	50	55	60	65	70	75		80	85	90					
T.B.S. in lbs.			18.7	15	10	15	18	19.5	22	15.5		10.2	7.8	6					

The results of breaking strength tests on annealed and solvent treated specimens in the three binary systems are shown in Fig. 2. Each value plotted was the mean of at least six closely agreeing results.

2. Compression Strength.

Apparatus.—Compression strength was measured with a 5-ton Buckton tensile machine, adapted for compression measurements, by determining the load necessary to crush each specimen. In the first series of experiments (referred to as "continuous loading" experiments) the load was steadily increased until fracture occurred; in the second series ("intermittent loading" experiments), specimens were compressed at a series of increasing loads, each load being applied for thirty seconds, when it was released, and the length of the specimen measured with a screw gauge reading to 0.0001 inch.

Preparation of Specimens.—The specimens used were cast in cold $\frac{1}{2}$ -inch test-tubes, the casting melts being 25° above the respective freezing-points, and the test-tubes were completely filled. The middle portions of the thick rods thus obtained were sawn into suitable lengths, and these were trued up to 1 inch \pm 0.001 inch by polishing the ends on emery paper. Both annealed and unannealed specimens have been examined, and the annealing was done in closely fitting test-tubes under the same temperature conditions as with transverse breaking strengths. The usual solvent treatment with water, alcohol and ether was employed and the specimens were coated with paraffin oil.

Only the system $\text{NaNO}_3/\text{KNO}_3$ was examined by this method.

(a) **Continuous Loading Experiments.**—Under these conditions of loading a complete set of compression strengths has been determined for annealed specimens. Annealing for four days gave very consistent results, and in all cases the values were less than for unannealed specimens. Still lower compression strengths were obtained after fourteen days' annealing, but the values were relatively the same as those for four days (Fig. 3), and it is therefore concluded that the shorter period is sufficient. Figures obtained for unannealed specimens showed such specimens to be considerably stronger than those which had been annealed, but consistent crushing strength figures were not given.

TABLE II.—COMPRESSION STRENGTHS (C.S.) FOR THE SYSTEM $\text{NaNO}_3/\text{KNO}_3$
(Compositions expressed as weight per cent. of KNO_3 .)

(a) *Continuous Loading.*

1. *Specimens annealed for 4 days.*

% KNO_3	0	10	25	40	55	70	85	100
C.S. (lbs.)	320	1900	3700	2200	450	2100	1800	760

2. *Specimens annealed for 14 days.*

% KNO_3	0	10	25	40	55	70	85	100
C.S. (lbs.)	—	1650	2600	1650	160	900	750	—

3. *Unannealed specimens.*

% KNO_3	0	10	40	55	70	85	100
C.S. (lbs.)	350	2150	4800	1650	3700	3500	1100

(b) *Intermittent Loading.*

Specimens annealed for 4 days.

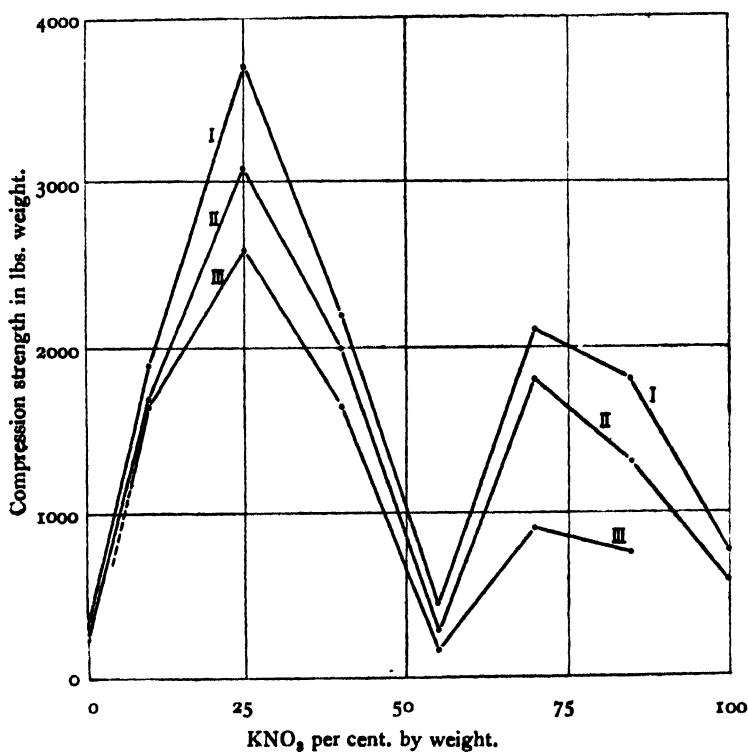
% KNO_3	0	10	25	40	55	70	85	100
C.S. (lbs.)	240	1700	3100	2000	290	1800	1300	580

(b) **Intermittent Loading Experiments.**—The length of each specimen, as measured after release of load, remained constant up to a small load (elastic limit), but thereafter a small but increasing permanent deformation occurred up to a certain load which varied with the composition of the mixture. Beyond this point considerable plastic flow set in and a further slight increase in load resulted in complete collapse of the specimen, the crushed material showing the typical cone-shaped fracture pieces similar to those obtained with crushed concrete. Fig. 4 summarises the data thus obtained.

In all cases the final crushing strengths were markedly lower than those obtained in the parallel experiments under continuous loading (see Fig. 3).

3. Brinell Hardness.

Apparatus and Method.—The hardness figures for each of the three systems have been determined, using an "Avery" Hardness Testing



- I. 4 days' annealing (continuous loading).
 II. 4 days' annealing (intermittent loading).
 III. 14 days' annealing (continuous loading).

FIG. 3.—Compression strength/composition diagram for the system $\text{NaNO}_3/\text{KNO}_3$.

TABLE III.—BRINELL HARDNESS FIGURES (B.H.).

(Compositions expressed as weight per cent. of the component stated.)

Series I.— NaNO_3 with KNO_3 .															
% KNO_3	.	.	0	10	25	40	55	70	85	100					
B.H.	.	.	3.0	13.1	28.2	25.8	1.6	28.2	14.3	8.8					
Series II.— $\text{Pb}(\text{NO}_3)_2$ with NaNO_3 .															
% NaNO_3	.	90	85	80	75	70	65	60	57.7	55	50	45	40		
B.H.	.	10.0	11.8	13.7	16.7	19.4	16.7	11.8	8.6	17.4	18.8	19.4	17.4		
Series III.— $\text{Pb}(\text{NO}_3)_2$ with KNO_3 .															
% KNO_3	.	95	90	85	80	75	70	65	60	55	50	45	40	35	
B.H.	.	.	1.9	2.7	2.7	3.5	4.3	7.4	10.9	11.8	10.9	8.6	10.9	11.8	10.9

Machine by measuring the diameter of the impression made by a 10 mm. steel ball. Small loads, varying between 10 and 50 Kgms., were used, and the period of loading was 300 seconds.

Specimens (1 inch diam. $\times \frac{1}{2}$ inch thick) were cast in cold nickel crucibles, and the melts used were poured at 25° above the respective freezing-points. Both of the flat surfaces of the annealed specimens were polished parallel before testing. Solvent treatment was applied as

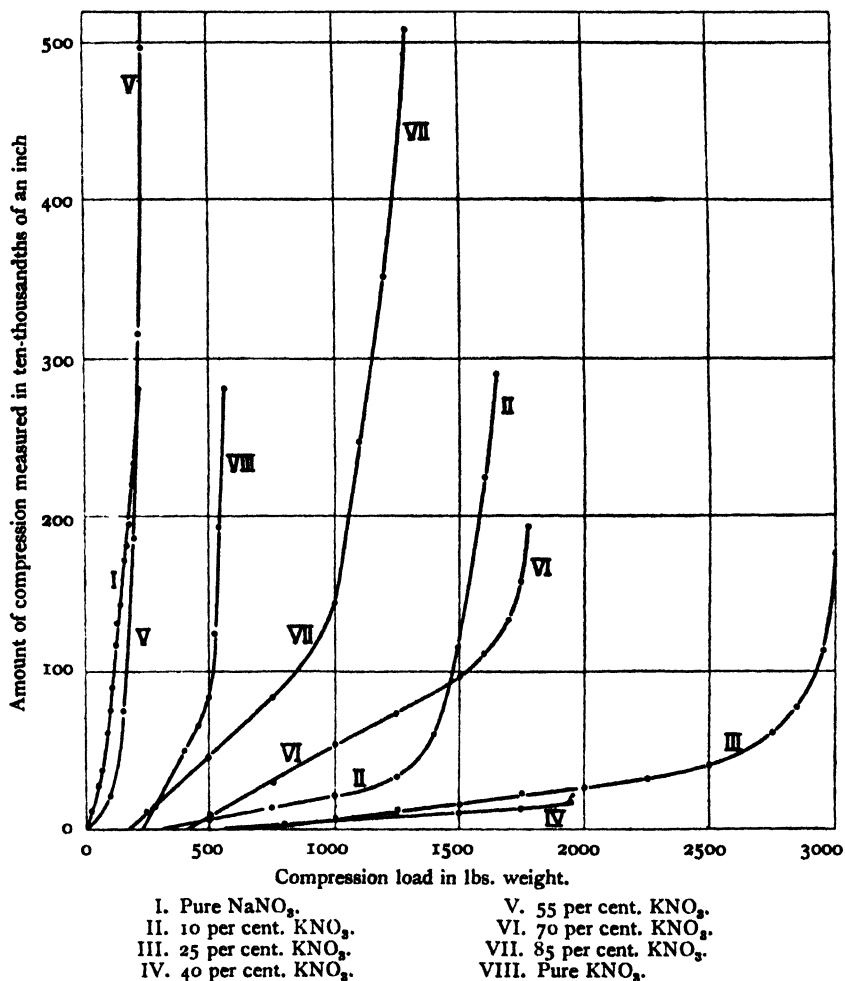


FIG. 4.—Compression/load diagram for the system $\text{NaNO}_3/\text{KNO}_3$ intermittent loading experiments.

before, but a paraffin oil coating was not applied, as it rendered the impression difficult to measure.

Owing to the dull white colour and the softness of the material, the impression marks were not always well defined. In view of this and the fact that no protective oil coating was used, the same degree of precision and accuracy cannot be claimed for these tests as for transverse breaking strength and compression strength measurements. Nevertheless, Brinell

hardness evidently varies widely with composition, and the general nature of this variation is the same in all the three systems.

Brinell hardness was calculated from the formula :

$$\text{B.H.} = \frac{L}{1.57D[D - \sqrt{D^2 - d^2}]}$$

where :

L = Load in Kilograms.

D = Ball diameter (10 mm.).

d = Diameter of impression in mm.

The results are shown in Fig. 5.

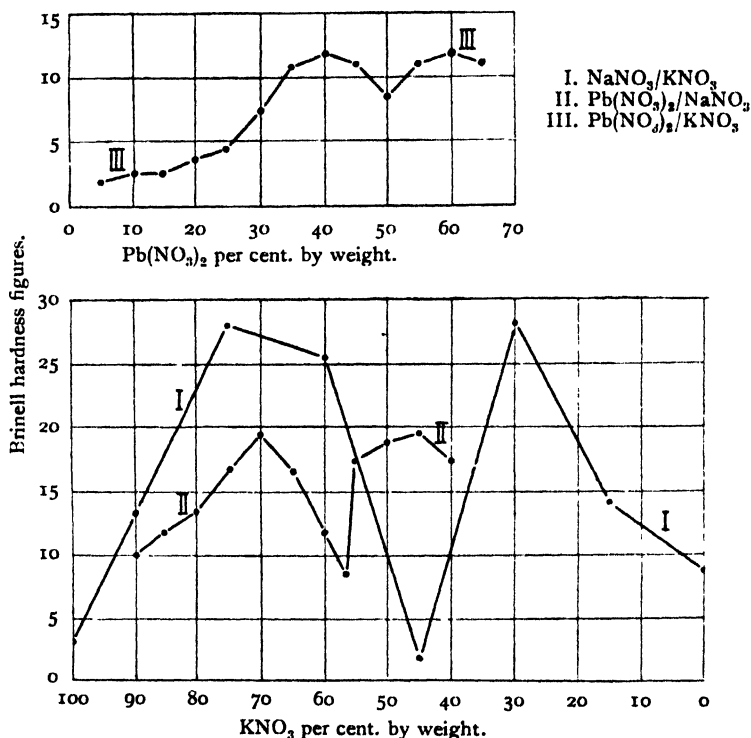


FIG. 5.—Brinell hardness/composition diagrams for the systems $\text{NaNO}_3/\text{KNO}_3$, $\text{Pb}(\text{NO}_3)_2/\text{NaNO}_3$ and $\text{Pb}(\text{NO}_3)_2/\text{KNO}_3$.

Discussion and Conclusions.

It appears from the work now recorded that any examination of mechanical properties of inorganic salt mixtures demands :

- Carefully regulated conditions of temperature for casting specimens.
- Adequate annealing of specimens.
- Solvent treatment, followed by application of a protective oil coating.

The authors are of opinion that there are surface effects removed largely by solvent treatment, and volume effects, which can only be

removed by annealing. It may be expected that annealing would not only relieve the internal strains set up during cooling, but would also promote the well-known phenomena of grain-growth, with consequent weakening of the structure, and this would explain the fact that values for annealed specimens are always markedly less than those for un-annealed specimens.

The surface effects have already been ascribed to the influence of atmospheric moisture. It is thought that such moisture may produce a recrystallisation film of fine crystals which has a cementing effect on the surface; solvent treatment would remove such a film. Minute surface cracks have been quoted as a source of weakness, and the increased strength of rock salt under water has been explained by some as a result of the removal of such cracks.⁷ In the results now reported a pronounced weakening has been caused by solvent treatment, and it therefore seems unlikely that the repair of surface cracks can be other than an insignificant factor by comparison with the cementation effects of atmospheric moisture.

In the three systems examined, the results are evidently of the same general type, and do not afford a means to distinguish a eutectic from a solid solution system. The curves (Figs. 2, 3 and 5) are of the form which Kurnakow¹ associates with partially miscible solid solutions, and in the case of the system $\text{NaNO}_3/\text{KNO}_3$ this agrees with Tammann's conclusion⁸ that mixtures of these two salts segregate on cooling. However, the two systems containing lead nitrate show behaviour somewhat different from that anticipated by Kurnakow, who has concluded that the property/composition curve should be a straight line for eutectic systems. In the present work, for certain intermediate mixtures values have been found which are much greater than would correspond with such a straight line relationship, although the actual eutectic mixtures have values very similar to those of the pure components. The authors find that the form of the curves is not altered by subjecting the specimens to as much as fourteen days' annealing.

The present results may possibly be explained in terms of internal strain. When mixtures of not exactly eutectic composition solidify, crystals of one pure component first separate and, at a lower temperature, eutectic solid forms as a magma in which the primary crystals are embedded. The setting of the eutectic magma between the primary crystals would be expected to set up a condition of strain, with a resulting hardening effect in the solid mass.⁹ Such a hardening effect should reach a maximum for compositions lying between the eutectic composition and the pure components, a conclusion which is amply supported by the results obtained in the present investigation. In the case of a solid solution system there are similar intermediate compositions of high internal strain where complete diffusion has probably not occurred on setting. In such a system, however, segregation in the solid state can take place on cooling, and in the resultant miscibility gap a condition of mere mechanical mixture is approached, with a corresponding weakening of the structure.¹⁰ Unless segregation were quite complete, the two-peaked type of curve would thus persist.

⁷ Cf. Desch, *Trans. Faraday Soc.*, **24**, 53, 1928.

⁸ *Z. anorg. Chem.*, **197**, 65, 1931.

⁹ Cf. Sachs, *Z. Metallk.*, **17**, 85, 1925.

¹⁰ Cf. Vršhesnevsky, *J. Russ. Phys. Chem. Soc.*, **43**, 1364, 1911.

Summary.

Transverse breaking strength, compression strength, and Brinell hardness figures have been measured for the systems $\text{NaNO}_3/\text{KNO}_3$, $\text{Pb}(\text{NO}_3)_2/\text{NaNO}_3$, and $\text{Pb}(\text{NO}_3)_2/\text{KNO}_3$. Property/composition diagrams are of the same general form in all three systems, and an explanation of this, in terms of internal strains developed during crystallisation, is put forward. It is claimed that atmospheric moisture produces surface hardening which is removable by solvents. The special conditions of casting, annealing and surface treatment necessary to obtain consistent results are stated.

We wish to thank Professor C. J. Hawkes for facilities which enabled us to carry out Brinell and compression tests, and Mr. C. E. Pearson for his helpful advice.

*Armstrong College (University of Durham),
Newcastle-upon-Tyne.*

THE SURFACE TENSION OF MERCURY IN A SILICA APPARATUS.

BY R. S. BURDON.

(Communicated by E. K. RIDEAL.)

Received 10th October, 1932.

The appearance of another paper on the surface tension of mercury may seem to call for an explanation or apology. The knowledge of the free surface energy of mercury in vacuum, however, is important, and firstly as data in any theory of surface-structure of liquid metals. Secondly workers making determinations of surface tension on other liquid metals frequently resort to mercury to test the consistency and accuracy of their methods, and finally the quantity is fundamental in any discussion of the experimental data on adsorption on a mercury surface.

On seeking this information some years ago in order to discuss certain phenomena presented by liquids spreading on mercury it was found impossible to obtain any agreement among the very many papers, and more recent work cannot be said to have lessened the confusion. Considering only papers appearing during the last ten years (in which period satisfactory vacuum technique may be expected) values are found to range from less than 400 dynes per cm. to considerably over 500 dynes. The variations in values obtained by different methods is not more marked than in those of different workers using the same method. Moreover, when using the same experimental methods workers have used formulæ giving as much as 10 per cent. variation in values calculated from identical data. Finally the recent work of Cook¹ and Kernaghan² using the method of the large drop, gives values differing by about 80 dynes per cm. although each appears to use essentially the same technique and formula for calculation.

It is thought that the present work does enable the value of the surface tension of mercury in vacuum to be fixed fairly closely and does account

for some prevailing discrepancies. In particular it is shown that values obtained using the method of the large drop are in reasonable agreement with those of workers using other methods.

In addition to the uncertainty of the value for vacuum there is the fact that many observers³⁻⁵ have found the surface tension of a large drop of mercury freshly formed in a gas to be as much as 100 dynes higher than that of a drop formed in vacuum. Popesco,³ in general agreement with earlier workers, found that the initial elevation of the surface tension for drops formed in a gas was approximately proportional to the pressure and that the value fell to that for vacuum or lower with continued exposure to the gas. Drops formed in vacuum maintained a constant value, while the admission of a gas after the drop was formed did not cause any rise in surface tension (toward the value for a drop formed in a gas) but on the contrary produced a further lowering.

Now from considerations of free energy it is inconceivable that any normal process of adsorption should account for the higher value in a gas, and Popesco and Perucca explain these facts in terms of the orientation of the molecules. They hold that in a mercury surface formed in a vacuum the molecules are at once turned to the position of minimum energy but that this orientation is delayed by the presence of the gas. Iredale⁶ considers the low value in vacuum probably due to some contamination which is adsorbed immediately in vacuum but more slowly in the presence of a gas. The bearing of the present work on these points will be discussed later.

The "Large Drop" Method.

The method used in this work has been that of the sessile drop used by many workers since Quincke.⁷ A large drop of the liquid is formed in either a cup-shaped depression or on a plane or concave surface, and the vertical distance, h , is measured between the summit B (Fig. 1) and the point A where the tangent to the surface is vertical (frequently called the equator). Thus measurements are not made on the part of the drop in contact with the solid and results should be independent of the properties of any substance other than the liquid, whereas most methods involve measurements depending on the contact of mercury and other substances.

At the equator the curvature is sharp and a small lamp a metre or more from the drop and on the same horizontal level gives a highly astigmatic image in the curved surface. In the reading microscope used this showed as a sharp horizontal line. (In an instrument of long focus it would appear as a star.) A change of 1 cm. in the height of the lamp caused less than 0.01 mm. change in the position of the image so that settings on A could be made with great precision.

The summit of the drop was defined by a parallel beam of light coming from the opposite side to the observer and the microscope was set on the apparent top of the drop. By setting up a similar drop on a glass disc in the open air, bringing a spherometer point almost into the surface and setting on the point and its reflection it could be checked that the method used did give the true summit. The parallel light gives a series of very sharp diffraction lines above the surface, but a test showed that these could not be used to locate the mercury surface. Various methods have been used by workers to define the top of the drop, but as pointed out elsewhere,⁸ it is very necessary to check that the illumination used does define the true summit. In particular, as

mercury is an almost perfect reflector it cannot be defined, nor indeed seen, by rays of light reflected from the surface.

The height h is about 0.28 cm. but the horizontal distance between A and B may be several centimetres. This involves moving the microscope between settings on these points and consequent risk of altering the height of the instrument during movement. (If the instrument is of sufficiently long focus to require no horizontal movement between the settings there will still be an error unless absolute horizontality of the optical axis is attained.) The writer used a method employed by some earlier workers. A piece of $\frac{3}{4}$ -in. plate glass was selected, tested against a 5-in. optical flat and found to possess the requisite plane surface. It was sealed to a slate table by a cement of plaster of Paris and kalsomine. This set sufficiently slowly to allow of the plate being levelled using a Pratt and Whitney 12-in. level. The level of the plate was found not to alter throughout the work. The Cambridge reading microscope mounted on rounded studs was pushed bodily to and fro to bring A and B into focus in turn, the focussing screw being untouched. The method proved satisfactory and the horizontality of movement was shown by setting on the surface of water on a large dish filled above the brim when the microscope could be caused to slide across the slab without changing the setting on the water surface. The accuracy of setting on surface or equator was about .002 mm.

Experimental Test of Formula.

If the drop is infinitely large (*i.e.*, has no curvature perpendicular to the plane of the diagram, Fig. 1), then the tension on a strip 1 cm.

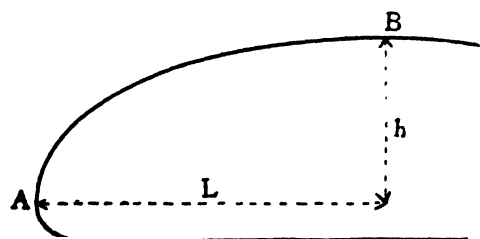


FIG. 1.

wide at B may be regarded as supporting the total horizontal thrust on the strip down to A , where the tangent is vertical. This gives at once

$$\sigma = \rho gh \times h/2 = \frac{1}{2} \rho gh^2,$$

the formula used by most workers. As long ago as 1885 Worthington⁹ drew attention to the fact that

the formula was inadequate for drops of the size actually used. Firstly, if the drop is not flat at B but has a total curvature x/R this will increase the hydrostatic pressure at A by an amount $2\sigma/R$ and hence reduce the observed value of h . Worthington stated that this correction is very small for drops of diameter 4 cm. or greater.

Secondly, the drop is curved in a plane at right angles to the principal section shown in the diagram, the radius of curvature being L (maximum radius of the drop) at A and increasing for higher points. This curvature of the surface means an added pressure inside the surface thus partly supporting the hydrostatic pressure and making h greater than for an infinitely large drop. Worthington makes an integration of this effect from A to B and obtains an expression which may be reduced to

$$\sigma = \frac{1}{2} \rho gh^2 \frac{(1.641L)}{(1.641L + h)}$$

for drops having L greater than 2 cm. The correction is of the order of 10 per cent.

Worthington recalculated some of Quincke's results, but more recent workers have frequently been unaware of Worthington's paper while those employing his correction have in general worked with drops of one size only. In order to discuss the results of different workers, therefore, it is very desirable to have direct experimental proof of the formula over the range of drops used. For this purpose distilled water in air was used since its surface tension is known and is not subject to large variations. One of my senior students, Mr. H. S. Gibson,¹⁰ using the microscope and illumination system set up for mercury, made observations on drops of water in freshly turned paraffin dishes up to 12 cm. in diameter, and also at the mid-point of the side of a large rectangular dish. His work shows that for drops over 2 cm. in radius the correction for R is negligible. For drops from 1.9 to 6 cm. in radius the formula above gives the same value, 71.8 dynes, within the limit of experimental error, while the uncorrected values range from 82.5 for the smallest, to 75 dynes for the largest drop. Moreover, observations by the capillary rise method agreed to within one-half of 1 per cent. with determinations by the method of the large drop.

For drops below 4 cm. diameter the variation is more rapid and the correction less simple. Gibson's work shows that for a diameter very close to 1.5 cm., the effect of curvature of the summit just neutralises that of horizontal curvature, and h is the same as for an infinitely large drop. As h is varying rapidly with diameter in this region it is not advisable to use drops of this size, but the result is of interest because Iredale,¹¹ who used the uncorrected formula, happened to use drops of about 1.5 cm. diameter, and so his striking results may be compared (at least approximately) with those of other workers.

Apparatus and Experimental Detail.

The essential part of the apparatus, shown between C and D (Fig. 2) was made by the Thermal Syndicate under instruction from Dr. M. L. Oliphant, and is entirely of water-clear fused silica. The flask, P , and liquid air trap, M , are also of silica. The possibility of using an apparatus entirely of quartz eliminates the risk of contamination by alkali from glass which some workers have suggested as a cause of the irregularities observed. The disc G was ground and polished, and the two windows, K , give no trace of distortion in any direction. The quartz apparatus was connected to pump, gauge, and special cut-off by a ground joint (not lubricated), the joint being covered by a plastic seal of pure rubber strip bound on and coated externally with cement. The Langmuir pump gave a vacuum beyond the limit of the MacLeod gauge (having a reservoir of 300 c.c.), and in addition special gas-absorption charcoal was used in the liquid air trap.

The apparatus was cleaned with hot chromic acid for some time, then washed and kept full of distilled water for some days, and finally washed many times by boiling distilled water in it. It was then completely sealed together so it could be dried out and tested before admitting the mercury.

The mercury after distillation stood for some days under water to which sodium peroxide was added at intervals. It was then shaken with chromic acid, thoroughly washed with distilled water and kept under

distilled water till required. Before putting it into flask *P*, it was twice distilled in a slow current of air.

On each of several days the apparatus was pumped out while being heated for two or three hours with a large pressure-torch. To avoid the chance of contaminated air leaking through the pumping system, dried and filtered air was admitted overnight through a mercury cut-off having no lubricated taps. Finally asbestos shields were placed round the quartz and, with the pressure-torch, the whole was maintained at a high temperature for three hours, each part in turn being brought to red heat again and again.

The apparatus was then filled with dry filtered air, the flask, *P*, opened, mercury put in, the flask again sealed, and the whole apparatus exhausted and heated with the torch, the whole operation taking less than half-an-hour. Mercury was then distilled under high vacuum and practically without ebullition into *E* and the apparatus sealed at *C*, with the pumps working throughout.

Liquid air was then placed round the charcoal and mercury distilled over to *F*, whence it flowed down the capillary tube and on to the quartz

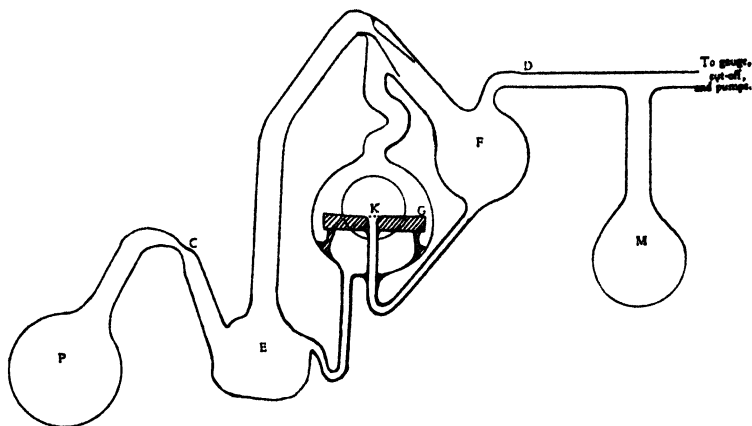


FIG. 2.

disc, *G*. Readings were taken with the drop at the maximum size of the disc (5 cm. diameter) and again, after causing a little of the mercury to spill over. Then more mercury was distilled till the drop again reached the limit of the disc and the readings repeated.

The mean value obtained was 488 dynes per cm. and the highest reading 491 dynes at laboratory temperature 25° C. (More precise fixing of temperature is unnecessary since surface tension and density vary in the same direction with the temperature and an error of as much as 5° C. causes less than 1 dyne error in the calculated surface tension.)

Subsequent Experiments.*

After standing filled with air for some time (owing to unavoidable interruption) the apparatus was evacuated, degassed and sealed at *D*.

* A preliminary set of experiments was performed to work out details of technique, and observations taken during this work gave values close to 470 dynes. On one occasion the apparatus contained a leak that would reduce the vacuum from X-ray to one showing fluorescence in a few minutes, yet with the pumps turned off the liquid air and charcoal held the vacuum against the leak for 18 hours—giving good X-ray vacuum at the end of that period.

If the quartz still contained impurity or was not perfectly degassed it was expected that the mercury would show a progressive lowering of surface tension. Readings were taken at intervals for some weeks, involving the same mercury being distilled over and over again. The values throughout ranged between 470 and 480 dynes indicating that conditions were not so good as during the main experiment, but there was no progressive falling in the value throughout the period. When a considerable number of drops were distilled over in succession on any one day the readings showed a slight progressive rise through a range of about 5 dynes. Iredale records a similar effect but with a much greater range of variation.

Six weeks after sealing off, the apparatus was enclosed in a heater and raised to 250°C . several times in making a determination of the temperature coefficient. Thereafter, readings at laboratory temperature still gave 475 dynes and a drop left standing on the disc for 4 days showed no change in height. Finally readings were taken on drops formed by tipping the apparatus (the part between *C* and *D*, Fig. 2) so that the mercury flowed round through the tubes from *E* through *F* and on to the plate when the same value was obtained. These observations showed firstly that the "clean-up" was sufficiently good that heating to 250°C . after standing evacuated for weeks did not cause any detrimental evolution of gas, and secondly that there was no detectable difference between the mercury in *E* and that distilled at high vacuum from *E*.

Temperature Coefficient.

If the surface were affected by an adsorbed layer it might be expected that this would show itself in some variation in temperature coefficient at higher temperatures.

The sealed quartz apparatus (*C* to *D*) was enclosed in an oven consisting of an inner brass case, $\frac{1}{4}$ inch thick, surrounded by asbestos lagging, $\frac{3}{4}$ inch thick, the whole enclosed in an outer case of sheet brass. Two small windows permitted the drop to be measured as usual. The windows of the quartz apparatus were cleared of condensed mercury by a small special heater for that purpose. The heat was supplied slowly by a heater of nichrome wire inside the oven. The heavy inner case of brass was designed to maintain an even distribution of heat by conduction though it was not expected to attain great precision owing to small local variations of temperature causing evaporation from the drop. Actually the method proved satisfactory; readings taken during the preliminary experiment to test the rate of heating, etc., gave a fall of 51 dynes between 20°C and 250°C . or just over .22 dyne per cm. per degree Centigrade.

Fig. 3. shows a set of readings up to 230°C . The temperature coefficient appears constant through that range of temperature, the value from the graph being .23 dynes per degree, which agrees with the preliminary readings practically within the limit of experimental error.

Surface Tension in Air.

It was long accepted that a large drop of mercury formed in the presence of a gas had a much higher surface tension than one formed in vacuum.^{3, 4} Observations made here in 1926 on mercury in a glass apparatus supported this view. The apparatus stood connected to

drying tubes for some months, and on starting to use it in 1927 the writer found that freshly formed drops showed very small differences in tension for all pressures of air down to an X-ray vacuum. Cook¹ obtained a higher value in vacuum than in air but there is general agreement that the tension falls in the presence of gases, and most rapidly at first, so that the method of forming the drop slowly as the mercury condenses does not necessarily give the maximum value for a drop freshly formed in a gas. To gain further data observations were made on each occasion after opening the sealed quartz apparatus, the drops being formed by tipping the apparatus as previously explained.

(a) **During Preliminary Work.**—Drops formed rapidly in laboratory air gave initial values slightly higher than drops distilled in vacuum just before opening the apparatus. The rate of decrease of surface tension with time of exposure to air was extremely slow at first, but after several days when the air in the apparatus had been exchanged

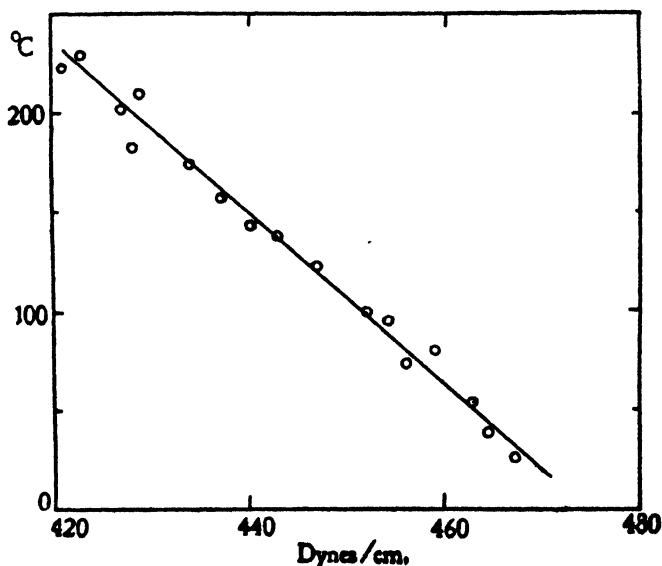


FIG. 3.

several times with no precautions against contamination the drops decreased in tension much more rapidly after formation.

(b) **After Main Experiment.**—The apparatus was opened and then connected by clean pressure tube to the pump and the laboratory air replaced by air drawn through a large flask containing stick caustic potash and a filter of glass wool sprinkled with phosphorous pentoxide. The value 480 dynes was obtained consistently and a drop left on the disc overnight showed a fall of only 4 or 5 dynes. On re-exhausting with the backing pump there was no fall in surface tension and drops poured in this vacuum gave the same value, 480 dynes.

The apparatus was then filled with air that had bubbled through distilled water. The value for freshly formed drops was still 480 dynes, falling 6 dynes in half-an-hour.

After refilling a number of times with wet air the rate of fall increased to 30 dynes in half an hour, but the value for a drop poured in vacuum

remained 480 dynes. Finally some water was placed in the apparatus and allowed to stand for a day. Thereafter in air the value fell from 480 to 430 dynes in half an hour. On pumping out to a moderate vacuum (so there would still be much water vapour present) the value for a newly formed drop was 482 dynes and the rate of decrease much the same as for wet air.

(c) **Experiments with Glass Apparatus.**—Using the glass apparatus with wax seals described in a former paper,¹² many observations were made of the rate of fall with exposure to air. Measurements were taken alternately filling the apparatus with air through a train of drying tubes and with air directly from the laboratory through a by-pass. In dry air the rate of fall was in approximate agreement with Popesco's figures,³ while in laboratory air the surface tension fell about three times as quickly during the first five minutes after forming the drop.

Discussion.

Surface Tension in Vacuum.

Owing to their large free surface energy it is to be expected that liquid metals would be very liable to contamination. In the absence of systematic error the highest value obtained may be considered most likely to be correct and in spite of the efforts made the value may be even higher than 488 dynes, the figure obtained in this work. Cook¹ gives a figure as high as 515 dynes, but an independent check on the method of measuring h seems desirable. Kernaghan has published the most recent determination by this method. The measurements indicate high precision and the value obtained at 20° C. was 436.1 dynes. The apparently extraordinary agreement of this with some earlier results (*e.g.*, Popesco's value, 436.3 dynes) is merely coincidence, since Popesco used drops 3.6 cm. in diameter and did not use Worthington's correction. When the correction is applied, Popesco's figures for h and L yield a value of approximately 400 dynes. Kernaghan's original paper left some doubt as to the method of defining the summit, but in a recent communication¹³ the author claims that this has been effectively checked.

A review of recent work, however, does afford much evidence that the surface tension of mercury in the vacuum is not far from 480 dynes/cm.

(a) Iredale⁶ obtained the value 475 dynes by the drop-weight method and later,¹¹ using large drops about 1.5 cm. in diameter (for which the Worthington correction is very small), obtained approximately the same value.

(b) The present work shows close agreement between the value for vacuum and for a drop freshly formed in dry air. Cook also found the highest values observed for surfaces formed in a gas approached those for vacuum. Work by Harkins and Ewing,¹⁴ as well as observations made here,¹² show that determinations by drop-weight give only very small differences between the values in vacuum and dry air. Hence it seems certain that the value actually obtained in dry gases, provided the time of exposure is not too long, should be very nearly the true value for vacuum. In this connection it is interesting that the highest value quoted by Popesco, 540 dynes for a large drop freshly formed in nitrogen corresponds to approximately 490 dynes when corrected for size of drop according to Worthington's formula.

Bircumshaw's recent work,¹⁵ using the method of maximum bubble pressure with dry hydrogen, gives 480 dynes at 20° C.

(c) Harkins and Ewing's¹⁴ value by the drop-weight method in vacuum is 476 dynes at 20° C., though in a later paper Harkins and Roberts¹⁶ quote the value 479.7 dynes at 40° C. (equal to 489 dynes at 20° C.). There is thus at least approximate agreement between the results obtained by different methods, and the agreement of Iredale, Cook, and the writer in obtaining a high value in vacuum by the large drop method shows that the low values previously observed by many workers were not necessarily due to the vacuum, nor could they be explained by the hypothesis of orientation of the molecules.

Temperature Coefficient.

Very few determinations in vacuum appear to have been made over any appreciable temperature range. Rideal¹⁷ quotes figures from a paper by Harkins and Roberts,¹⁶ giving a temperature coefficient 0.233 dyne per degree and constant from 40° C. to 170° C. This is in remarkable agreement with the present work, but the paper referred to is a compilation and the source of the experimental data was not discovered. Harkins and Ewing,¹⁴ by the drop-weight method in vacuum between 0° C. and 60° C., obtained the value .22 dyne per degree. Bircumshaw's¹⁵ figures yield this value also for the bubble-pressure measurements from 20° C. down to within a few degrees of the freezing-point of mercury.

The present work (Fig. 3) does not indicate any departure from the linear relation up to 230° C., but it seems certain the temperature coefficient must increase at higher temperatures, or the critical point of mercury would be impossibly high. Kernaghan² appears to have made the only other determination by the large drop method, but this author's figure, 0.3015 dyne per degree, appears to be based on readings through the range 12° C. to 49° C. only. Four determinations given at higher temperatures (up to 67° C.) suggest a much lower coefficient. At present neither the critical point of mercury nor its surface tension at high temperatures is sufficiently well known to compare its behaviour with that of other liquids in respect to surface tension and critical data. Hogness¹⁸ and Hagemann obtain data up to 350° C. in hydrogen and water vapour respectively, and in each case there is a definite increase in temperature coefficient above 200° C.

Adsorption and the Variation of Surface Tension.

When a water surface is contaminated by a strongly adsorbed substance (e.g., stearic acid) there is little fall in the surface tension until the monomolecular layer is practically complete. Indeed it is difficult to picture the mechanism by which anything much less than a contiguous layer of molecules could appreciably affect the surface tension. The completion of this layer is marked by a large, comparatively sudden fall, and there is no evidence of adsorption beyond a single layer. Measurements on the surface of mercury have not shown these two well-defined levels. Reasonable agreement may be said to have been reached for the presumably uncontaminated surface. The low value in vacuum obtained consistently by various workers using the large drop method strongly suggests a complete adsorbed layer, but actually any value between the highest and lowest seems consistently obtainable if experimental conditions remain constant. The cause of the low value in vacuum recorded by Popesco and others remains unexplained.

As already explained the hypothesis of simple orientation of the mercury molecules to positions of minimum energy is untenable. Nor can the low value be dismissed as merely due to poor vacuum since the writer obtains high values for all pressures from atmospheric down to 10^{-6} mm., whereas Iredale obtains both the high value (*c.* 470 dynes) and a low value (*c.* 410 dynes) at a pressure of 10^{-5} mm. Iredale was unable to locate the source of contamination, and suggested it might be adsorbed elsewhere than from the vapour phase. This seems quite possible since a monomolecular layer contains about 6×10^{14} molecules per sq. cm., and at a pressure of 10^{-5} mm. these would occupy roughly

$$\frac{6 \times 10^{14}}{6 \times 10^{23}} \times 2.24 \times 10^4 \times \frac{760}{10^{-5}} = 1700 \text{ c.c.}$$

Hence it would require every molecule in many litres of vapour at 10^{-5} mm. to give a monomolecular layer over a large drop of mercury.

Observers generally agree that in the presence of a gas the surface tension falls most rapidly at first, and approaching a rather indefinite lower limit after some hours. The work of Oliphant²⁰ shows that drops of mercury, after falling a few centimetres in hydrogen containing 2 per cent. carbon dioxide, are covered with a practically complete layer of the CO_2 . This appears to show firstly, that the monomolecular layer is absorbed within a very small fraction of a second, certainly before the surface tension has fallen measurably, and secondly, that the life of the adsorbed hydrogen molecule is short compared with that of the CO_2 molecule. Cook, however, reports that the value for a large drop in hydrogen at 0.00015 mm. pressure remained constant at 421 dynes, but that on breaking the surface the tension rose to 473 dynes and the gas evolved brought the pressure up to 0.00048 mm. This is more compatible with a long life of the adsorbed molecule on the surface, and the large increase in surface tension on breaking the surface (presumably removing the gas layer), when contrasted with the very small fall during the initial adsorption, leaves scope for much speculation as to processes occurring subsequent to the adsorption of the first layer. The present work indicates the need of more experimental evidence as a basis for any theory. In particular the failure to observe the customary fall in surface tension in air on first opening the intensely dried quartz apparatus, coupled with the fact that the value did fall "normally" after some days when the air had been changed repeatedly, suggests the possibility that, in spite of care, the actual cause of the lowering may be something carried in by the air rather than the air itself. If this were so the large area of clean quartz surface might absorb practically all the contamination from the air first admitted leaving the mercury unaffected, whereas any action due to the bulk of air itself would begin immediately the air was admitted. Attempts to prove that the lowering is due to water vapour failed here as did those of Iredale who at first suspected that it was the cause of the low value in vacuum.

Hence it may be said that very little is known of the action of gases on a mercury surface, and unambiguous results are difficult to obtain owing to uncertainty as to the part played by the walls of the apparatus in absorbing and evolving gas. The suggestion that the fall in surface tension in gases may be due to some undetected agent gains a certain amount of support from the marked difference in the rate of fall for filtered and unfiltered air recorded above. Moreover, Kazda²¹ and

Dunn²² found that the photo-electric threshold for a moving mercury surface was unaffected by the presence of small pressures of various gases, but that tap-grease sealed in a side tube surrounded with liquid air would affect the threshold value within a few minutes of removing the liquid air. This observation indicates adsorption from the vapour phase, but a danger in photo-electric threshold might well occur with much less than a monomolecular layer of contamination.

Conclusion.

The value of the surface tension of mercury in vacuum is found to be 488 dynes/cm. and to be the same for a drop freshly formed in air. The tension falls by 0.23 dyne per degree and linearly (very nearly) up to 230° C. Work up to the present does not admit of a positive conclusion as to the action of gases on a mercury surface. The possibility of orientation and re-arrangement occurring in the surface layer after the initial adsorption of a gas layer would afford a plausible explanation of the facts at present known, but there is no experimental proof that this actually happens.

The writer would express his thanks to Professor Kerr Grant for his interest in the work and his assistance in obtaining the apparatus, to Dr. M. L. Oliphant and the Thermal Syndicate for the skilful design and execution of the silica work, and to Mr. R. H. Oliphant for much assistance in getting the apparatus together.

Adelaide,
June, 1932.

REFERENCES.

- ¹ Cook, *Physic. Rev.*, **34**, 513, 1929.
- ² Kernaghan, *Physic. Rev.*, **37**, 990, 1931.
- ³ Popesco, *Ann. Physique*, **3**, 402, 1925.
- ⁴ Perucca, *Phil. Mag.*, **7**, 418, 1929.
- ⁵ Stoeckle, *Wied. Ann.*, **66**, 499, 1898.
- ⁶ Iredale, *Phil. Mag.*, **48**, 177, 1924.
- ⁷ Quincke, *Phil. Mag.*, April 1871.
- ⁸ Burdon, *Nature*, **129**, 456, 1931.
- ⁹ Worthington, *Phil. Mag.*, **20**, 51, 1885.
- ¹⁰ Gibson. (*In the press.*)
- ¹¹ Iredale, *Phil. Mag.*, **49**, 608, 1925.
- ¹² Burdon and Oliphant, *Trans. Far. Soc.*, **23**, 205, 1927.
- ¹³ Kernaghan, *Nature*.
- ¹⁴ Harkins and Ewing, *J.A.C.S.*, **42**, 2539, 1920.
- ¹⁵ Bircumshaw, *Phil. Mag.*, **12**, 596, 1931.
- ¹⁶ Harkins and Roberts, *J.A.C.S.*, **44**, 656, 1922.
- ¹⁷ Rideal, *Surface Chemistry*, p. 20.
- ¹⁸ Hogness, *J.A.C.S.*, **43**, 1621, 1921.
- ¹⁹ Hagemann, *Diss. Freiburg*, 1914.
- ²⁰ Oliphant, *Phil. Mag.*, **6**, 422, 1928.
- ²¹ Kazda, *Physic. Rev.*, **26**, 643, 1925.
- ²² Dunn, *Physic. Rev.*, **29**, 639, 1927.

THE ENERGY OF THE GROUND STATE OF METHANE.

BY H. J. WOODS (*Textile Physics Laboratory, The University, Leeds*).

Received 13th October, 1932.

In a recent paper Slater¹ has given an approximate solution of the problem of the determination of the energy of the ground state of a polyatomic molecule, valid provided that the bonds are definitely of the "electron-pair" type. This would be the case for the bonds formed by tetravalent carbon, according to the ideas of Pauling² and Slater,³ who show that the existence of directed valencies is due to the type of atomic eigenfunction which it is necessary to use in molecular problems. According to them, the correct functions to take for the valence electrons of the ⁶S carbon atom are not the usual atomic ones ($2s$, $2p_0$, $2p_{+1}$, and $2p_{-1}$), but that set of linear combinations of the four *which makes the energy of the molecule a minimum*. This leads, in the case of carbon, to four "tetrahedral" functions, each "pointing out" in the direction of one of the corners of a regular tetrahedron at whose centre the nucleus lies. The bound atoms then arrange themselves in such positions that the valence eigenfunction of each "overlaps" one of the carbon functions as much as possible. Since the interaction of two electrons is determined by the amount of this overlapping, the above procedure makes the interaction between those electrons whose functions overlap very strong, and at the same time weakens that between these electrons and the other ones in the atoms concerned. The contribution to the energy of the molecule due to the interaction of any pair of atoms joined by a bond is thus due largely to a single pair of electrons. If the spins are now distributed in such a way that these contributions are negative, and so lead to attractions between the atoms, then a state is reached in which the energy of the molecule is as small (algebraically) as possible; in other words, the energy so obtained is that of the ground state of the molecule.

The appropriate carbon eigenfunctions are

$$\left. \begin{aligned} \Psi &= Ar(1 + 3 \cos \theta)e^{-\frac{1}{2}\frac{r}{a_0}} \\ \Phi &= Ar(1 - \cos \theta + 2\sqrt{2} \sin \theta \cos \phi)e^{-\frac{1}{2}\frac{r}{a_0}} \\ \chi &= Ar(1 - \cos \theta - \sqrt{2} \sin \theta \cos \phi + \sqrt{6} \sin \theta \sin \phi)e^{-\frac{1}{2}\frac{r}{a_0}} \\ \Theta &= Ar(1 - \cos \theta - \sqrt{2} \sin \theta \cos \phi - \sqrt{6} \sin \theta \sin \phi)e^{-\frac{1}{2}\frac{r}{a_0}} \end{aligned} \right\} \quad (1)$$

where a_0 is the radius of the first Bohr circle.

In these, the co-ordinates are referred to the carbon nucleus as origin. The atomic functions from which they are derived are of the Slater type.⁴

¹ Slater, J. C., *Physic. Rev.*, **38**, 1109, 1931.

² Pauling, L., *J. Am. Chem. Soc.*, **53**, 1367, 1931.

³ Slater, J. C., *Physic. Rev.*, **37**, 481, 1931.

⁴ *Ibid.*, **36**, 57, 1930.

z is a constant representing the effective nuclear charge of the carbon atom; its value is 3.25 according to Slater, although Zener,⁵ by a variational method, finds the value $z = 3.18$. In what follows, the value $z = 3.2$ has been taken.

The function Ψ has a maximum, for constant r , along the line $\theta = 0$; Φ along the line $\phi = 0$, $\theta = \cos^{-1}(-\frac{1}{3})$, and so on for the others. Each function is symmetrical about its maximal direction; and each may be derived from Ψ by a rotation through the tetrahedral angle.

In CH_4 , the hydrogen nuclei are placed on the axes of the four functions. Calling them a, b, c and d , a is placed on the axis of Ψ (the z -axis), b on the axis of Φ , c on that of χ , and d on that of Θ . The four hydrogen eigenfunctions are represented by α, β, γ , and δ respectively. All eight functions are normalised; this, of course, determines the value of the constant A in (1). The four carbon functions are, in addition, mutually orthogonal, as is easily seen from their forms.

If the eight electrons are numbered 1, 2, . . . 8, then the "overlap" integral

$$S_{\alpha\Psi}^2 = \int \alpha_1 \Psi_1 \alpha_2 \Psi_2 d\tau_1 d\tau_2 \quad (2)$$

and the similar ones $S_{\beta\Phi}^2$, $S_{\gamma\chi}^2$, and $S_{\delta\Theta}^2$, are made large by the assumption of the form (1) for the carbon eigenfunctions, whereas the integrals like

$$S_{\alpha\Phi}^2 = \int \alpha_1 \Phi_1 \alpha_2 \Phi_2 d\tau_1 d\tau_2 \quad (3)$$

are made small.

Using Slater's method, the energy of the molecule may be written

$$E = \frac{\int U^* H U d\tau}{\int U^* U d\tau} \quad (4)$$

where U is the molecular eigenfunction constructed in the usual way from the functions Ψ, α, \dots , satisfying the necessary symmetry conditions. The integrals include summation over the spin co-ordinates. The spins of Ψ and α are opposite, as are those of the other pairs of overlapping functions. U thus has the form *

$$U = \Sigma \pm \begin{vmatrix} \bar{\Psi}_1 & \bar{\Psi}_2 & \dots & \bar{\Psi}_8 \\ \alpha_1 & \alpha_2 & \dots & \alpha_8 \\ \bar{\Phi}_1 & \bar{\Phi}_2 & \dots & \bar{\Phi}_8 \\ \beta_1 & \beta_2 & \dots & \beta_8 \\ \dots & \dots & \dots & \dots \\ \delta_1 & \delta_2 & \dots & \delta_8 \end{vmatrix}$$

where the summation is over the sixteen different ways of distributing the spins amongst the four pairs. The spins of the functions are denoted by the bars placed above or below them.

H is the Hamiltonian for the complete molecule,

$$H = -\frac{\hbar^2}{8\pi^2 m} \sum_{i=1}^8 \nabla_i^2 + \sum_a \frac{Ze^2}{R_a} + \sum_{ab} \frac{e^2}{R_{ab}} + \sum_{i < j} \frac{e^2}{r_{ij}} - \sum_{a, i} \frac{e^2}{r_{ai}} - \sum_{i=1}^8 \frac{Ze^2}{r_i} \quad (5)$$

⁵ Zener, C., *Physic Rev.*, **36**, 51, 1930.

* The signs preceding the determinants are such that interchanging the spins of any two overlapping functions changes the sign of U , which is therefore antisymmetric in the spins of each pair of bond functions.

where $R_a = R_b = R_c = R_d$ is the $C-H$ distance (the symmetrical molecule only is considered) ;

$R_{ab} = R_{bc} = \dots$ is the $H-H$ distance ;

r_i = distance of electron i from the carbon nucleus ;

r_{ij} = distance between the electrons i and j ;

r_{ai} = distance of electron i from a ;

and Z = the effective charge of the carbon core.

Instead of using the Hamiltonian in this form, it is convenient to split it up into the sum

$$H = H_0 + H_a + H_b + H_c + H_d + V \quad . \quad . \quad (6)$$

where H_0 is the Hamiltonian for the carbon atom, $H_a, \dots H_d$ are those for the isolated hydrogens, and V is the perturbing potential due to the proximity of the five atoms.

Since $(\Psi\Phi\chi\Theta)$ is a solution of the wave equation for the carbon atom,

$$H_0(\Psi\Phi\chi\Theta) = E_0(\Psi\Phi\chi\Theta) \quad . \quad . \quad . \quad (7)$$

E_0 being the energy of the 4S state of the atom. Similarly

$$H_a(\alpha) = E_a(\alpha) \quad . \quad . \quad . \quad (8)$$

and so on for each of the other hydrogens.

Then

$$\begin{aligned} H(u_0) &= H(\Psi_1\alpha_2\Phi_3 \dots \delta_8) \\ &= E'u_0 + Vu_0 \end{aligned} \quad . \quad . \quad . \quad (9)$$

where $E' = E_0 + \Sigma E_a$, and $u_0 = \Psi_1\alpha_2\Phi_3 \dots \delta_8$. . . (10)

u_0 is a function of the positional co-ordinates of the electrons only. If $u_r = P_r(u_0)$, P_r being a permutation of the electron space co-ordinates, then

$$\begin{aligned} \int u_r H u_0 d\tau &= \int (u_r E' u_0 + u_r V u_0) d\tau \\ &= E' \int u_r u_0 d\tau + \int u_r V u_0 d\tau \end{aligned} \quad . \quad . \quad (11)$$

these integrals being over the space co-ordinates. Now, when the integrals in E are expanded in terms of the eigenfunctions, E takes the form

$$\begin{aligned} E &= \frac{\Sigma \eta_r \int u_r H u_0 d\tau}{\Sigma \eta_r \int u_r u_0 d\tau} \\ &= E' + \frac{\Sigma \eta_r \int u_r V u_0 d\tau}{\Sigma \eta_r \int u_r u_0 d\tau} \end{aligned} \quad . \quad . \quad (12)$$

where η_r is a coefficient depending on the spin properties of U . The values of these coefficients can be found by application of the rules given by Slater¹ for the manipulation of mixed functions of the spin and positional co-ordinates.*

For any u_r , we have, since the atomic functions are normalised,

$$\int u_r V u_0 d\tau = (E_c - E_{c_r}) \int u_r u_0 d\tau + \int u_r V_r u_0 d\tau \quad . \quad . \quad (13)$$

* For the case $u_r = \Psi_1\alpha_1\Phi_2\beta_2\chi_2\gamma_2\Theta_2\delta_2$, the coefficient has the value $+16 \times 8!$; when $u_r = \Psi_1\alpha_1\Phi_1\beta_1\chi_1\gamma_1\Theta_1\delta_1$, it is $-8 \times 8!$. For convenience, the factor $16 \times 8!$ is taken out of both numerator and denominator of the fraction, so that the η 's in these two cases are $+1$ and -1 .

where V_r is the sum of the terms in V involving the co-ordinates of the electrons which are permuted by P_r , and E_{c_r} is the sum of the corresponding coulomb energy terms,

$$E_{c_r} = \int u_0 V_r u_0 d\tau \quad . \quad . \quad . \quad (14)$$

$E_c = E_{c_0} = \int u_0 V u_0 d\tau$ is the mutual coulomb energy of the five atoms. From (12), therefore,

$$E - E' = E_c + \frac{\sum \eta_r [\int u_r V_r u_0 d\tau - E_{c_r} \int u_r u_0 d\tau]}{\sum \eta_r \int u_r u_0 d\tau} \quad . \quad . \quad (15)$$

It is necessary now to examine the contributions to the fractional part of (15) due to the various permutations P_r . If $u_r = u_0$, the contribution is evidently zero. For the simple transposition of a pair of bond electrons (say 1 and 2) the term in the numerator of the fraction is

$$E_{12} = e^2 \left[-S_{\alpha\psi}^2 \left\{ \int \frac{\Psi_1^2 \alpha_2^2}{r_{12}} d\tau_1 d\tau_2 - Z \int \frac{\alpha_2^2}{r_2} d\tau_2 - \int \frac{\Psi_1^2}{r_{a_1}} d\tau_1 \right\} \right. \\ \left. + \left\{ \int \frac{\Psi_1 \Psi_2 \alpha_1 \alpha_2}{r_{12}} d\tau_1 d\tau_2 - Z S_{\alpha\psi} \int \frac{\Psi_1 \alpha_1}{r_1} d\tau_1 - S_{\alpha\psi} \int \frac{\Psi_1 \alpha_1}{r_{a_1}} d\tau_1 \right\} \right] \\ + e^2 \left[-3S_{\alpha\psi}^2 \int (\Psi_2^2 + \alpha_2^2) \beta_4^2 \left(\frac{1}{r_{24}} - \frac{1}{r_{b_4}} \right) d\tau_2 d\tau_4 \right. \\ \left. + 3S_{\alpha\psi} \int 2\Psi_2 \alpha_2 \beta_4^2 \left(\frac{1}{r_{24}} - \frac{1}{r_{b_4}} \right) d\tau_2 d\tau_4 \right] \\ \left. + e^2 \left[-3S_{\alpha\psi}^2 \int \frac{\alpha_2^2 \Phi_3^2}{r_{23}} d\tau_2 d\tau_3 + 3S_{\alpha\psi} \int \frac{\alpha_2 \Psi_2 \Phi_3^2}{r_{23}} d\tau_2 d\tau_3 \right] \right] \quad (16)$$

The first part of this is the value which would be obtained by the Heitler and London method, in the absence of the rest of the hydrogen atoms and the other carbon electrons; the presence of the former introduces the terms in the second bracket, and the terms in the third bracket are due to the three remote carbon electrons. It is easily seen that these have a much greater effect than the hydrogens; the protons and electrons of the hydrogen atoms give contributions of opposite signs and of approximately the same numerical value, whereas there is no such compensation in the other bracket. It is clear, however, that the carbon electrons give a contribution which is in the opposite direction to that of the nucleus in the first bracket, and we may hope to approximate to the value of (16) by adjusting the value of Z in order to compensate for the effect of the three remote electrons.

The value of the exchange term in (15) corresponding to a transposition of two hydrogen electrons is much smaller than (16). The principle part of it is the ordinary Heitler-London value for the interaction of two hydrogen atoms. To this must be added a correction due to the carbon atom and one due to the remaining hydrogen atoms, the former predominating.

In the case of the transposition of a hydrogen electron and one of the remote carbon electrons (*e.g.*, 2 and 3) the exchange term consists firstly of the ordinary two-electron value, then a correction due to the carbon electrons other than 3, and finally one due to the remaining hydrogens, which is smaller. The whole of this term is small in comparison with (16), owing to the smallness of the overlap integral $S_{\alpha\phi}^2$.

If the values of the integrals $S_{\alpha\psi}^2$, $S_{\alpha\phi}^2$, and $S_{\alpha\beta}^2$ were so small that their squares could be neglected, then the exchanges discussed above would be the only ones of importance (the integral for the exchange of 1 and 3 vanishes, since $S_{\psi\phi}^2 = 0$). But $S_{\alpha\psi}^2$ has been made large; its value in the region of the equilibrium distance is in the neighbourhood of 0.5. This makes it necessary to consider certain other types of exchange, *i.e.*, those in which there are transpositions in more than one bond simultaneously. For example, the permutation which interchanges 1 and 2 and at the same time 3 and 4 leads to integrals of the order $S_{\alpha\psi}^4$; the exchange term, therefore, is certainly not negligible compared with (16). The terms which will be taken into account are those due to permutations which consist either of transpositions of the pairs of bond electrons alone, or of such transpositions combined with at most one exchange between electrons which are not paired in a bond. Permutations involving the interchange of two pairs of hydrogen electrons are omitted, as are all cyclic ones.

First consider the effect of all those exchanges in which there are only transpositions in the bonds. There will be four of the simple type considered above in which only one pair of bond electrons transpose. Then there will be six in which two pairs of bond electrons undergo transpositions at the same time. In four others, three pairs are concerned, and finally there is one term in which all the bonds experience exchanges.* The sum of the terms corresponding to all these permutations is $(1 + S_{\alpha\psi}^2)^3$ times the value for the simple exchange, E_{12} , together with a correction due to the fact that certain terms are taken into account twice instead of once. In full, the sum is

$$E'_{12} = 4(1 + S_{\alpha\psi}^2)^3 E_{12} + 6S_{\alpha\psi}^4 (1 + S_{\alpha\psi}^2)^2 e^2 \left[\int \frac{\Psi_1^2 \beta_4^2 + \alpha_1^2 \beta_4^2 + \alpha_1^2 \phi_4^2}{r_{14}} d\tau_1 d\tau_4 \right. \\ \left. - \frac{2}{S_{\alpha\psi}} \int \Psi_1 \alpha_1 (2\beta_4^2 + \phi_4^2) \frac{1}{r_{14}} d\tau_1 d\tau_4 + \frac{3}{S_{\alpha\psi}^2} \int \frac{\Psi_1 \alpha_1 \phi_4 \beta_4}{r_{14}} d\tau_1 d\tau_4 \right] \quad (17)$$

In order to obtain an estimate of the size of the correction, it is assumed that, approximately,

$$\frac{\frac{1}{S_{\alpha\psi}} \int \frac{\Psi_1 \alpha_1 \beta_4^2}{r_{14}} d\tau_1 d\tau_4}{\int \frac{\alpha_1^2 \beta_4^2}{r_{14}} d\tau_1 d\tau_4} = \frac{\frac{1}{S_{\alpha\psi}^2} \int \frac{\Psi_1 \alpha_1 \phi_4 \beta_4}{r_{14}} d\tau_1 d\tau_4}{\frac{1}{S_{\alpha\psi}} \int \frac{\alpha_1^2 \phi_4 \beta_4}{r_{14}} d\tau_1 d\tau_4} \\ = \frac{\frac{1}{S_{\alpha\psi}} \int \frac{\Psi_1 \alpha_1 \phi_4^2}{r_{14}} d\tau_1 d\tau_4}{\int \frac{\alpha_1^2 \phi_4^2}{r_{14}} d\tau_1 d\tau_4} = 1 + k \quad (18)$$

Then if

$$\frac{\int \frac{\Psi_1^2 \beta_4^2}{r_{14}} d\tau_1 d\tau_4}{\int \frac{\alpha_1^2 \beta_4^2}{r_{14}} d\tau_1 d\tau_4} = 1 + k', \quad (19)$$

* The values of the η 's are the same for all these permutations.

the value of the expression in the square brackets in (17) is

$$-k(2k' - 3k) \int \frac{\alpha_1^2 \beta_4^2}{r_{14}} d\tau_1 d\tau_4 \quad (20)$$

The value of k cannot be found exactly; but noting that

$$\int \frac{\beta_4^2 \alpha_1^2}{r_{14}} d\tau_1 d\tau_4 < \int \frac{\beta_4^2 \Psi_1 \alpha_1}{S_{\alpha\Psi} \cdot r_{14}} d\tau_1 d\tau_4 < \int \frac{\beta_4^2 \Psi_1^2}{r_{14}} d\tau_1 d\tau_4 \quad (21)$$

we have

$$I < I + k < I + k'. \quad (22)$$

At $R_a = 2a_0$, the value of k' is 0.30, and therefore the value of k , which will lie somewhere near the middle of the range defined by (22), will not be very much different from 0.15. Using this value, the size of the correction terms in (17) is only about 1 per cent. of E_{12} , and the error in the total energy due to the neglect of the correction will be only half as great. It appears then that the correction is not very important, although, of course, the discussion given above can at best only lead to an estimate of the order of magnitude of the error.

Similarly, the sum of those terms in (15) which are due to exchanges including the transposition of two hydrogen electrons is found to be

$$E'_{24} = 12S_{\alpha\beta}^2(I + S_{\alpha\Psi}^2)E_{12} + 6(I + S_{\alpha\Psi}^2)^2E_{24} \quad (23)$$

apart from small corrections of the same type as those in E'_{12} . In this, E_{24} is the exchange term for the simple transposition of two hydrogen electrons, obtained from the first bracket of (16) by writing β and $S_{\alpha\beta}$ instead of Ψ and $S_{\alpha\Psi}$, and putting $Z = 1$, together with the corrections mentioned in the previous discussion of this term.

For the exchanges which include a transposition of a hydrogen electron and one of the remote carbon electrons, the total contribution is

$$E'_{23} = 24S_{\alpha\phi}^2(I + S_{\alpha\Psi}^2)E_{12} + 12(I + S_{\alpha\Psi}^2)^2E_{23} \quad (24)$$

where E_{23} is the value for the simple exchange.

The coefficient η_r has the value $+1$ in (17) and $-\frac{1}{2}$ in (23) and (24). Thus the numerator of the fraction in (15) is

$$4g^3\{(1 - \frac{3}{2}g^2S_{\alpha\beta}^2 - 3g^2S_{\alpha\phi}^2)E_{12} - \frac{3}{2}gE_{24} - \frac{3}{2}gE_{23}\} \quad (25)$$

where $g = (1 + S_{\alpha\Psi}^2)^{-1}$. The value of the denominator is easily seen to be $g^4(1 - 3g^2S_{\alpha\beta}^2 - 6g^2S_{\alpha\phi}^2)$. The expression for the energy is thus

$$E - E' = E_c + 4 \frac{(1 - \frac{3}{2}g^2S_{\alpha\beta}^2 - 3g^2S_{\alpha\phi}^2)E_{12} - \frac{3}{2}gE_{24} - \frac{3}{2}gE_{23}}{g(1 - 3g^2S_{\alpha\beta}^2 - 6g^2S_{\alpha\phi}^2)} \quad (26)$$

In E_{12} , the terms due to the hydrogen atoms will be neglected. As far as can be judged by a method similar to that adopted above in the case of the correction in (17), this will only introduce an error of about 1 per cent. in the total energy. The influence of the remaining carbon electrons in (16) is to be accounted for by an adjustment of the nuclear charge, as mentioned above. The amount of this shielding is estimated in the following way: the correction terms represent the potential of the distribution of density α^2 in the field of the distribution ϕ^2 diminished

by the mutual potential of the distributions Φ^2 and $\frac{\Psi\alpha}{S_{\alpha\Psi}}$. Now in the first bracket of (16) the terms due to the nucleus represent its energy in the field of α^2 diminished by its energy in the field $\frac{\Psi\alpha}{S_{\alpha\Psi}}$. Thus the new value of Z must be chosen so that the potentials of α^2 and $\frac{\Psi\alpha}{S_{\alpha\Psi}}$ in the field of the unshielded nucleus and the three carbon electrons are the same as in the field of Z . This cannot be done exactly by giving Z any one value, owing to the difference between the two distributions, but an approximation can be obtained by making the shielding exact for the electron, at each $C-H$ distance. The shielding for the other distribution is probably not very different, since the greater penetration of the electron distribution into that of the remote carbon electrons will be counterbalanced by the concentration of $\frac{\Psi\alpha}{S_{\alpha\Psi}}$, whose maximum lies nearer to the carbon nucleus than that of α^2 .

The correction terms in E_{24} are neglected, and its value is taken to be that for the isolated atoms. In the case of E_{23} the effect of the remaining carbon electrons is too great to be omitted, so that a correction must be applied to account for their influence. Since, however, the form of the integrals in E_{23} will, as mentioned below, prohibit its evaluation by the usual methods, we cannot hope to do more than estimate the probable size of the whole term. If a similar assumption to that made above in the case of E_{12} is also made in this case, i.e., that the effect of the other carbon electrons can be represented by an appropriate reduction in the nuclear charge, then the value of E_{23} is obtained by writing Φ instead of Ψ and $S_{\alpha\Phi}$ instead of $S_{\alpha\Psi}$ in the first bracket of (16), where Z will now have a new value. The integral

$$J_{23} = \int \frac{\Phi_2 \alpha_2 \Phi_3 \alpha_3}{r_{23}} d\tau_2 d\tau_3 \quad (27)$$

whose evaluation is made difficult by the presence of the azimuth in Φ , is the only one in the expression which gives any trouble. Its value is, presumably, positive, whereas the rest of the expression is negative, so that an upper limit to the value of $|E_{23}|$ can be obtained by omitting J_{23} altogether. At $R_a = 2a_0$, this gives

$$2E_{23} = 1.33E_{24} \quad (28)$$

On the whole, then, the contribution to the energy due to $2E_{23}$ will be of the same order as that due to E_{24} . An idea of the importance of E_{23} can be obtained by comparing the values of the energy in the two extreme cases, $E_{23} = 0$ and $J_{23} = 0$.

Apart from the integral J_{23} , the only one presenting any difficulty is

$$J_{12} = \int \frac{\Psi_1 \alpha_1 \Psi_2 \alpha_2}{r_{12}} d\tau_1 d\tau_2 \quad (29)$$

This was evaluated by the method given in detail by Rosen,⁶ who has systematised the calculation of the integrals occurring in molecular problems, and whose tables of the functions involved considerably

⁶ Rosen, N., *Physic Rev.*, **38**, 255, 1931; **38**, 2099, 1931.

884 THE ENERGY OF THE GROUND STATE OF METHANE

lighten the labour of the arithmetical computations. All the other integrals in this problem can be evaluated by elementary methods.

The integrals were computed at the three points, $R_a = 1.75a_0$, $2.0a_0$, and $2.25a_0$. Omitting E_{23} the energy is a linear function of the nuclear charge Z , regarding this as a parameter in E_{12} (the coulomb energy can be found exactly). It is therefore easy to find the energy for any value of this effective charge by calculating it for two values of Z and interpolating. The coulomb energy of a hydrogen electron has its correct value in the field of the shielded nucleus for the effective charges $Z = 1.64$, 1.56 , and 1.49 , at $R_a = 1.75a_0$, $2.0a_0$, and $2.25a_0$ respectively. Using these values in the first bracket of (16), the energy, omitting the contribution from E_{23} comes out as

$$\frac{1}{2}(E - E') = \left. \begin{array}{l} -0.196 e^2/a_0 \text{ at } R_a = 1.75a_0, \\ -0.196 e^2/a_0 \text{ at } R_a = 2.0a_0, \\ -0.173 e^2/a_0 \text{ at } R_a = 2.25a_0. \end{array} \right\} \quad (30)$$

and

From these the equilibrium distance is $R_a = 1.88a_0 = 1.01 \text{ \AA.U.}$, and the energy at this distance is -5.3 volts.

By putting $J_{23} = 0$, an upper limit for the energy is obtained. The values so found are:—

$$\frac{1}{2}(E - E') = \left. \begin{array}{l} -0.176 e^2/a_0 \text{ at } R_a = 1.75a_0, \\ -0.182 e^2/a_0 \text{ at } R_a = 2.0a_0, \\ -0.162 e^2/a_0 \text{ at } R_a = 2.25a_0. \end{array} \right\} \quad (31)$$

and

These give a minimum at $R_a = 1.93a_0 = 1.04 \text{ \AA.U.}$, and an energy there of -4.9 volts. The values in (30) and (31) give the limits between which the energy must lie; the correct value of E_{23} lies between the values taken in the calculation of these figures.

The value usually taken for the energy of the $C - H$ bond is about -5.0 volts, measured from the excited 5S level of the carbon atom,⁷ so that both of the limits given above may be considered to be in good agreement with experiment. Mecke⁷ gives the $C - H$ distance in methane as 1.08 \AA.U. , and the values given here agree with this as well as can be expected in problems of this kind. The vibration frequency when all the hydrogens are moving towards or away from the carbon nucleus together is 3100 cm.^{-1} and 3300 cm.^{-1} in the two cases. The fundamental frequency of the $C - H$ bond is usually taken to lie between 2800 and 3000 cm.^{-1} .⁸

For reference, the following table gives the contributions to the energy due to the various terms, at the separation $R_a = 2a_0$. The figures under E_{23} give the upper limit to its value, and are obtained by neglecting J_{23} . The energies are those for a single bond, the totals for the molecule being four times as great.

E_c	Due to E_{12}	Due to E_{34}	Due to E_{23}	Total.
$-0.104 e^2/a_0$	$-0.104 e^2/a_0$	$0.011 e^2/a_0$	$0.015 e^2/a_0$	$\left\{ \begin{array}{l} > -0.196 e^2/a_0. \\ < -0.182 e^2/a_0. \end{array} \right.$

⁷ Mecke, R., *Z. physik. Chem.*, **7B**, 108, 1930.

⁸ Bhagavantam, S., *Nature*, **129**, 830, 1932.

The large contribution of the coulomb term is to be noted; it is more than 50 per cent. of the total, quite a different state of affairs from that in H_2 , where the coulomb energy is much smaller than the exchange energy.

The author wishes to express his thanks to Professor Lennard-Jones for reading the paper in manuscript, and for his valuable advice and criticism.

THE INHIBITION OF THE PHOTOCHEMICAL DECOMPOSITION OF AMMONIA BY ATOMIC HYDROGEN.

By H. W. MELVILLE.

Received 20th October, 1932.

It is now well recognised that molecules which exhibit diffuse absorption band spectra undergo dissociation on absorption of a quantum of radiation in a time much less than the interval between collisions at atmospheric pressure. Bonhoeffer and Farkas¹ pointed out that, owing to the nature of its absorption spectrum, the photo-decomposition of ammonia would involve the primary dissociation of the molecule into NH_2 and H. They showed that the absence of fluorescence of the NH_3 molecules was in accordance with this view. Several experiments were later carried out to prove the existence of hydrogen atoms during the decomposition of ammonia.

Farkas, Haber and Harteck² found that if ammonia is mixed with hydrogen and oxygen and illuminated with a zinc spark, combination of H_2 and O_2 occurs. At temperatures below $415^\circ C$. many molecules of H_2O were formed per NH_3 molecule decomposed, while explosion occurred above 415° and 300 mm. pressure, although H_2 and O_2 alone require to be heated to at least 440° for spontaneous explosive combination. Haber and Oppenheimer's observation³ that H atoms induce explosion in $H_2 - O_2$ mixtures below 440° appeared to indicate that the ammonia sensitised reaction must be due to initiation by H atoms.

Taylor and Emeléus⁴ discovered that just as atomic hydrogen, produced by the reaction $Hg(2^3P_1) + H_2$, induced polymerisation in ethylene, so on illuminating a $NH_3 - C_2H_4$ mixture polymerisation of the hydrocarbon took place. The products of the reaction, however, contained a considerable amount of nitrogenous substance. Hill and Vernon⁵ found that tungstic oxide was rapidly reduced in presence of illuminated ammonia.

These experiments are based upon analogy, and although they are very convincing on account of the simple molecular transformations involved, yet they are not direct proofs of the existence of atomic hydrogen since the part played by the reactive radical NH_2 has been neglected.

¹ *Z. physik. Chem.*, **134**, 337, 1928.

² *Z. Electrochem.*, **36**, 711, 1930.

³ *Z. physik. Chem.*, **16B**, 443, 1932.

⁴ *J. Amer. Chem. Soc.*, **53**, 562, 1931.

⁵ Cited by Taylor and Emeléus, *unpublished experiments*.

The second problem in the photochemistry of ammonia which required a direct proof was the low quantum yield. In a recent discussion of the question Wiig and Kistiakowski⁶ conclude that the most plausible explanation is recombination of the primary products of dissociation either by ternary collisions or at the walls. They suggest that surfaces prepared in a suitable way may inhibit or accelerate this recombination.

Similar problems arose during experiments on the photochemistry of phosphine. The absorption spectrum is of the predissociation type⁷ and the quantum yield is less than unity.⁸

In the mercury photosensitised decomposition of phosphine⁹ in presence of hydrogen a simple mechanism leads to the equation

$$1/R = 1/K \left(1 + \frac{k_2[H_2] + k_3}{k_1[PH_3]} \right),$$

R is the rate of decomposition, K is a constant, k_1 is the reaction velocity coefficient of PH_3 with 2^3P_1 Hg atoms, k_2 that for H_2 and k_3 the rate of deactivation of excited Hg atoms by radiation. On plotting $1/R$ against $[H_2]$, maintaining $[PH_3]$ constant, a straight line should be obtained. For low values of $[H_2]$ a linear relationship held good but as $[H_2]$ increased the curve began to tend upward, becoming convex to the $[H_2]$ axis. That is, the reaction velocity decreases at a rate which is greater than can be accounted for by simple deactivation of the excited mercury atoms by molecular hydrogen. Since atomic hydrogen is produced by this deactivation process it was natural to assume that H atoms were responsible and that the retardation was due to the reaction $PH_2 + H$ being accelerated owing to the artificial increase in the concentration of H atoms.

This tentative suggestion was verified by illuminating a $PH_3 - H_2$ mixture separately and simultaneously with a zinc spark and a water-cooled mercury arc lamp. The rate of decomposition with simultaneous illumination by spark and arc was less than that with separate illumination, which proved that in presence of atomic hydrogen the photodissociation of PH_3 was inhibited. At the low pressures used the recombination $PH_2 + H$ must occur at the walls.

On recalculating Mitchell and Dickinson's results¹⁰ on the mercury photosensitised decomposition of ammonia according to the above equation it was found that curves similar to those for phosphine were obtained as is shown by Fig. 1. This parallelism suggested that a confirmatory experiment might be made on the same basis as that for phosphine.

A zinc spark and a water-cooled mercury lamp were therefore set up close to a 7 cm.-diameter silica bulb attached to a McLeod gauge, liquid air traps, pumps and gas * reservoirs. The relative distance of spark and arc was so adjusted that the rates of the direct and photosensitised reactions in absence of hydrogen were about equal. Sufficient hydrogen to reduce the rate of the photosensitised reaction to a negligibly small value was then introduced. The rate of the direct reaction is not

⁶ *J. Amer. Chem. Soc.*, **54**, 1906, 1932.

⁷ Melville, *Nature*, **129**, 546, 1932.

⁸ Melville, *unpublished experiments*.

⁹ Melville, *Proc. Roy. Soc.*, A **138**, 374, 1932.

¹⁰ *J. Amer. Chem. Soc.*, **49**, 1487, 1927.

* The gases were saturated with mercury before entering the reaction bulb.

affected by molecular hydrogen, the experiments being made at room temperature. First of all the mixture is illuminated with the zinc spark and, after condensing out the ammonia with liquid air, the pressure of $N_2 + H_2$ measured. The arc is then switched on and, keeping the spark intensity constant, another exposure made of the same period, the pressure of $N_2 + H_2$ being again determined.

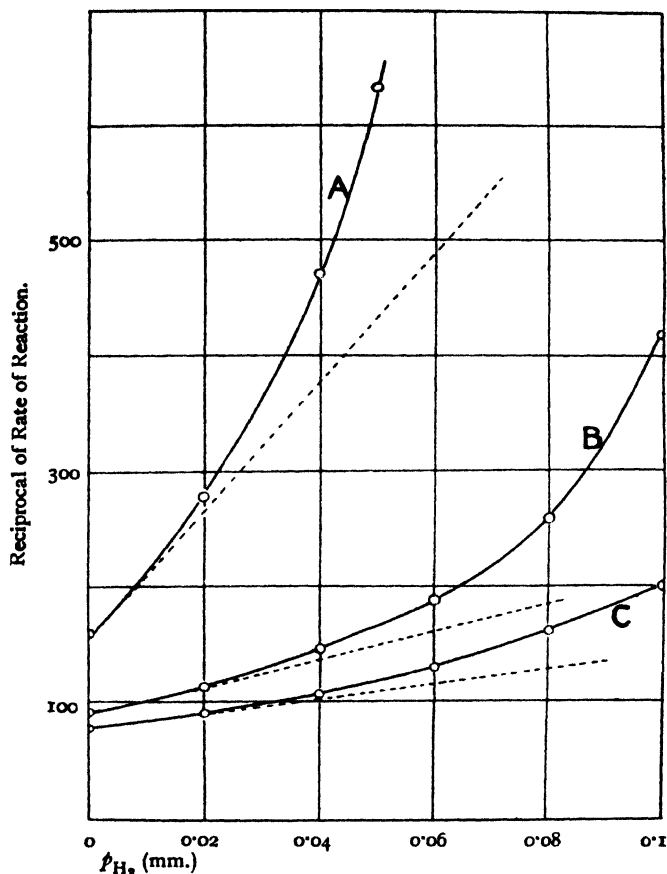


FIG. 1.—Mitchell and Dickinson's results for the photosensitized decomposition of NH_3 . The curves show that the reciprocal of the rate of decomposition increases more rapidly than p_{H_2} , the deviation being relatively greater at low NH_3 pressures.

A = $p_{NH_3} = 0.95$ mm.
 B = $p_{NH_3} = 1.88$ mm.
 C = $p_{NH_3} = 3.22$ mm.

The results of four typical series of experiments are shown in the Table below. When the mixture of ammonia and hydrogen is exposed to the arc alone, there is no pressure change and therefore no decomposition of ammonia. On illuminating the mixture with arc and spark simultaneously the pressure increase, *i.e.*, the pressure of $N_2 + H_2$ produced, is *less* than that with spark alone. The direct photochemical decomposition of ammonia is consequently retarded when the arc is switched on.

TABLE I.

Pressure of NH_3 , 0.3 mm. Room Temperature ca. 20° C.
 Rate of Hg sensitised reaction 0.0125 mm. $\text{N}_2 + \text{H}_2$ per 20 min. in absence of H_2 .

p_{H_2} mm.	Increase of Press.	Condition of Illumination.
0.0765 } 0.0765 } 0.0795 } 0.0865 }	0.000 0.003 0.007	after 20 min. exposure to arc " " " " arc + spark " " " " spark
0.0830 } 0.0830 } 0.0860 } 0.1030 }	0.000 0.003 0.0170	after 10 min. exposure to arc " 20 " " " arc + spark " 20 " " " spark
0.0860 } 0.0915 } 0.0925 }	0.0055 0.0010	after 15 min. exposure to spark " 15 " " " spark + arc
0.1030 } 0.1070 } 0.1080 }	0.0040 0.0010	" 10 min. exposure to spark " 10 " " " spark + arc

p_{H_2} includes the small amount of N_2 produced during the decomposition.

Retardation of the photosensitised reaction in presence of hydrogen is due to a reduction in the concentration of excited mercury atoms owing to collisions between H_2 molecules and Hg atoms in the 2^3P_1 state. This retardation is, however, simultaneously accompanied by the production of atomic hydrogen. It would appear that the inhibition is due to some reaction involving atomic hydrogen which regenerates ammonia.

Hydrogen atoms do not react with ammonia¹¹ or with N_2 ,¹² reaction must therefore occur with NH or NH_2 as these are the only possible intermediate products of the decomposition in a static system.^{4, 13} It is simpler to assume, having regard to the fact that molecular hydrogen is without influence on the reaction at 20° C., that retardation is due to the reaction $\text{NH}_2 + \text{H} = \text{NH}_3$, which occurs either by the participation of a third molecule or on the walls of the insolation tube in order to effect stabilisation of the NH_2 molecule.

Since the primary photo-dissociation of NH_3 can be represented by the equation $h\nu + \text{NH}_3 = \text{NH}_2 + \text{H}$, and as the above experiments indicate that the reverse reaction also occurs, then it is probable in absence of artificially introduced H atoms, *i.e.*, during the normal photo-reaction, the same reaction $\text{NH}_2 + \text{H} \rightarrow \text{NH}_3$ takes place. Hence

¹¹ Bonhoeffer and Boehm, *Z. physik. Chem.*, **119**, 385, 1926.

¹² Lewis, *J. Amer. Chem. Soc.*, **50**, 27, 1928.

¹³ Gedye, *J. Chem. Soc.*, 1160, 1932.

it may be concluded (a) that the low quantum yield in the direct decomposition of NH_3 is due to recombination of the primary products of dissociation, (b) that the inhibition by H atoms provides an additional direct proof that H atoms are one of the intermediate products of the reaction.

It is convenient in this communication to mention that the recombination hypothesis may be supported in another direction. If H or NH_3 could be removed sufficiently rapidly quantum yields of the order of unity might be obtained. The corresponding experiments have been carried out with phosphine, using oxygen to remove the products of dissociation, but the conditions are complicated by the intrusion of a chain mechanism. With ammonia conditions are less complex. Emeléus¹⁴ found that the rate of decomposition of ammonia is increased twofold in presence of carbon monoxide. Presumably the carbon monoxide is able to remove H or NH_2 or both before they have an opportunity to recombine.

These experiments were made during the tenure of a Carnegie Research Scholarship.

Summary.

An experiment is described in which it is shown that the direct photochemical decomposition of ammonia is inhibited by atomic hydrogen. The method consists in illuminating an NH_3 - H_2 -mercury vapour mixture with a zinc spark and with and without a water-cooled mercury arc lamp. With the Hg arc in operation the rate of the decomposition is retarded by the atomic hydrogen produced by the reaction $(2^3P_1) \text{ Hg} + \text{H}_2$. This experiment is advanced (1) as a proof of the dissociation of ammonia into hydrogen atoms, (2) as an explanation of the low quantum yield due to the reaction $\text{NH}_2 + \text{H} = \text{NH}_3$.

*Department of Chemistry,
University of Edinburgh.*

¹⁴ *These Transactions*, 28, 89, 1932.

THE BEHAVIOUR OF THE HYDROGEN ELECTRODE IN CHROMIC-CHROMOUS SOLUTIONS AND THE SOLUBILITY PRODUCT OF CHROMOUS HYDROXIDE.

BY W. H. BENNETT.

Received 20th October, 1932.

A knowledge of the behaviour of the hydrogen electrode in oxidation-reduction systems is of considerable importance, for the determination of their free acidity. A considerable amount of work on organic oxidation-reduction systems has been published by W. M. Clark and his co-workers,¹ but little had been done on inorganic systems of a similar type until Elder's recent paper² on the behaviour of various electrodes,

¹ W. M. Clark, *The Determination of Hydrogen Ions*, 1928, and *Chemical Reviews*, 2, 127, 1925.

² L. W. Elder, Jr., *Trans. Amer. Elect. Soc.*, 57, 383, 1930.

including the hydrogen and bright platinum electrodes in acid ferrous-ferric solutions. He showed that the hydrogen electrode behaved similarly to the bright platinum oxidation-reduction electrode and could be used to indicate the end points when a hydrochloric acid solution of ferrous and ferric chlorides was titrated with sodium hydroxide solution.

The work to be described was undertaken to see whether the hydrogen electrode or the polished platinum electrode could be used to indicate the end-points when a sulphuric acid solution of chromous and chromic sulphates was similarly titrated with caustic soda. The following results show that broadly the effect is the same in both cases. In the case of the solutions studied, basic sulphates were probably precipitated and the inflections were not sharp enough to give quantitative results, owing to the close proximity of the p_H values of precipitation of chromous and chromic hydroxides, and the extreme instability of chromous salt solutions which slowly decompose water with the evolution of hydrogen at ordinary temperatures.³ The titration curves obtained, interpreted in the same way as Elder's curves, enable an approximate value of the solubility product of chromous hydroxide to be calculated, a determination which does not appear to have been previously attempted.

Experimental.

Preparation of the Solution.

The chromous sulphate solution was prepared by electrolytic reduction of chromic sulphate solution (^{4,5}). A lead cathode was used made from a rectangular piece of thin sheet lead, 10.5×7.4 cm. in size, bent into a cylindrical shape, with a tab for a terminal. This was thoroughly cleaned in moderately strong nitric acid and the surface prepared according to the instructions of Tafel.⁵ This electrode was placed in a large porous pot, waxed to below liquid level and fitted with an air-tight waxed cork with two tubes passing through it, one to lead off the evolved hydrogen through a trap, the other to run off the reduced solution. The anode in the outer cell was of platinum gauze. A solution of chromic sulphate was prepared by stirring an excess of Kahlbaum pure crystalline chromic sulphate with water, in the cold, for some time and allowing it to stand. To 100 c.c. of this solution, 15 c.c. of concentrated sulphuric acid were added very slowly, the mixture being stirred and cooled in running water to avoid the formation of the green modification of chromic sulphate which is more difficult to reduce.⁴ The acid chromic sulphate solution was placed in the inner cell with 15 per cent. sulphuric acid in the outer cell. The liquid in the outer cell was covered with paraffin to keep air from diffusing through, and the whole was placed in a vessel of water kept cool by a spiral of lead pipe through which cold water flowed.

A current of 0.7 amp. was passed through the solution for forty-five hours. At the end of this period some of the chromium salt had diffused through the pot, and becoming oxidised, coloured the solution orange, but the solution in the porous pot which was blown out and kept tightly stoppered under $\frac{1}{2}$ inch. of paraffin, was deep blue. The concentration

³ Asmanov, *Z. anorg. Chem.*, **160**, 209, 1927.

⁴ Traube, Burmeister and Stahn, *Z. anorg. Chem.*, **147**, 50, 1925.

⁵ Tafel, *Z. physikal. Chem.*, **34**, 187, 1900.

of acid in the solution to be reduced appears high, but was adopted because a similar reduction carried out with the same current density for the same time with 3 per cent. sulphuric acid, resulted in most of the chromium being deposited on the cathode as a hard irregular mass of mixed chromium metal and oxides.

Analysis of the Solution.

A portion of the solution was diluted with air-free distilled water and portions equivalent to 2 c.c. of the original solution taken for analysis. The total content of chromium and sulphate was determined by adding bromine water to oxidise the chromous salt to chromic, boiling off the excess bromine and precipitating chromic hydroxide with ammonia in the presence of ammonium chloride in the usual way; dissolving the precipitate in hydrochloric acid, reprecipitating with the addition of some macerated filter paper, washing and igniting the precipitate to Cr_2O_3 . This method has been stated to give high results⁶ owing to the formation of higher oxides of chromium. In these cases the precipitated hydroxide had been dried and ignited, without the addition of filter pulp which would cause the ignited oxide to be hard and lumpy. It was found, however, that precipitation in the presence of filter pulp and subsequent slow ignition yielded a fine powdery oxide of theoretical composition. The filtrates obtained above were combined, adjusted to an acidity of $2\frac{1}{2}$ per cent. with hydrochloric acid and the sulphate precipitated with barium chloride, allowed to settle overnight, filtered, ignited and weighed as BaSO_4 . To determine the chromous content of the solution a portion was quickly pipetted into an excess of ferric alum solution acidified with sulphuric acid, and the ferrous iron formed titrated with standard potassium permanganate solution which had been standardised against A.R. ferrous ammonium sulphate. The colour of the chromium salts obscured the end-point to some extent, but if the titration was carried out in a beaker held a few inches above a brightly illuminated white tile the end-point was easily visible and readings agreed exactly with those obtained by potentiometric titration of the same solutions.

It was found that 2 c.c. of the reduced chromium solution contained 0.0911 gm. of chromous chromium and 0.0122 gm. of chromic chromium. This solution had to be standardised each time before use as it slowly oxidised, even in a stoppered bottle under $\frac{1}{2}$ inch of paraffin. For instance, after twenty days, 2 c.c. of the above solution contained 0.0886 gm. chromous chromium, and after fifty days, 2 c.c. of the same solution contained 0.0788 gm. chromous chromium.

Titration.

The titration cell was a wide-mouthed bottle, fitted with a waxed air-tight cork bored for the hydrogen or oxidation-reduction electrode, hydrogen exit, burette, stirrer, auxiliary electrode and hydrogen entrance, the latter being used only when the oxidation-reduction electrode was in use. The stirrer had a mercury seal so that the cell could be completely filled with hydrogen and remain air-tight. The hydrogen electrode was of the wire type, consisting of a piece of platinum wire sealed into the end of a thin glass tube and wound round the outside

⁶ See H. T. S. Britton, *Analyst*, 49, 130, 1924.

of the tube five or six times. The electrode was mounted in a wider tube down which hydrogen was blown so that 2 or 3 mm. of the spiral projected. It was platinised according to the instructions of Britton⁷ and checked against a phthalate buffer. This electrode was more convenient for this cell than the foil type and was quite satisfactory as long as the spiral was not allowed to project far out of the end of the tube, as slightly lower readings were then obtained, owing no doubt to the end of the wire becoming unsaturated with hydrogen. When it was adjusted so that only 2 or 3 mm. of the tip of the spiral projected into the liquid results were very reliable. The oxidation-reduction electrode was of bright platinum gauze and was thoroughly cleaned before each determination. A saturated calomel electrode connected by a saturated potassium chloride bridge was used as an auxiliary electrode. The *E.M.F.* was measured by the potentiometer-voltmeter method.⁸ The scale of the voltmeter was only graduated in centivolts but the *E.M.F.* could be estimated to within 2 millivolts, which is quite accurate enough for work on unstable solutions of this type.

The solution to be titrated was made by adding 5 c.c. of the stock chromous-chromic solution to 100 c.c. of air-free water, and duplicate solutions were titrated with 0.9111 *N*/5 NaOH with the hydrogen and bright platinum electrodes, the cell being filled with hydrogen. The solution was stirred after the addition of each portion of alkali, but not while the readings were being taken. The time taken to reach equilibrium varied from three to ten minutes, being greatest near the inflection points. Light green chromic hydroxide was precipitated first, followed by brownish-black chromous hydroxide. The point at which chromic hydroxide began to precipitate was easily noted by the appearance of a permanent turbidity in the solution and the commencement of the precipitation of chromous hydroxide was made evident by the blackening of the precipitate produced round each drop of caustic soda solution added. The titration cell was strongly illuminated from behind so as to make these changes easily recognisable.

A number of titrations were carried out. Owing to the instability of the solution its composition could not be kept constant and the curves exactly duplicated, but they were all the same shape and the general results obtained from each were similar. The one reproduced is typical of the series. The solution used in obtaining this curve contained 0.2215 gm. chromous chromium, 0.0368 gm. chromic chromium and 0.3214 gm. SO_4 in 105 c.c.

From this the theoretical end-points of the titration were calculated as 33.43 c.c., 45.08 c.c., and 91.86 c.c. of 0.9111 *N*/5 NaOH. The three vertical dotted lines X, Y and Z, in the diagram, correspond to these end-points and the two arrows indicate the points at which chromic and chromous hydroxides began to be precipitated. The slope of that portion of the curve corresponding to the precipitation of chromous hydroxide is greater than would be expected from theory. It is notable that the slopes of the curves obtained by Britton⁹ and Elder³ for the precipitation of $\text{Fe}(\text{OH})_2$ are abnormal, but no explanation of this effect is offered. In the present case the close proximity of the precipitation p_H values of $\text{Cr}(\text{OH})_3$ and $\text{Cr}(\text{OH})_2$ would no doubt influence the shape of the curve, as the two hydroxides might be precipitated

⁷ H. T. S. Britton, *Hydrogen Ions*, p. 35, 1932.

⁸ Sand and Law, *J. Soc. Chem. Ind.*, **30**, 3872, 1911.

⁹ H. T. S. Britton, *J.C.S.*, **127**, 2110-2159, 1925.

together near the inflection point. Again the explanation may lie in the disturbances in the *E.M.F.* of the hydrogen electrode due to the tendency of chromous salts to decompose with evolution of hydrogen, a reaction which is catalysed by platinum black.³ In both cases the divergence from the true value would be less as the $[Cr^{++}]$ diminished.

It will be evident from the shape of the curve that the end-points can only be roughly fixed by its aid. The first two inflections, giving the neutralisation point of the free sulphuric acid and the completion

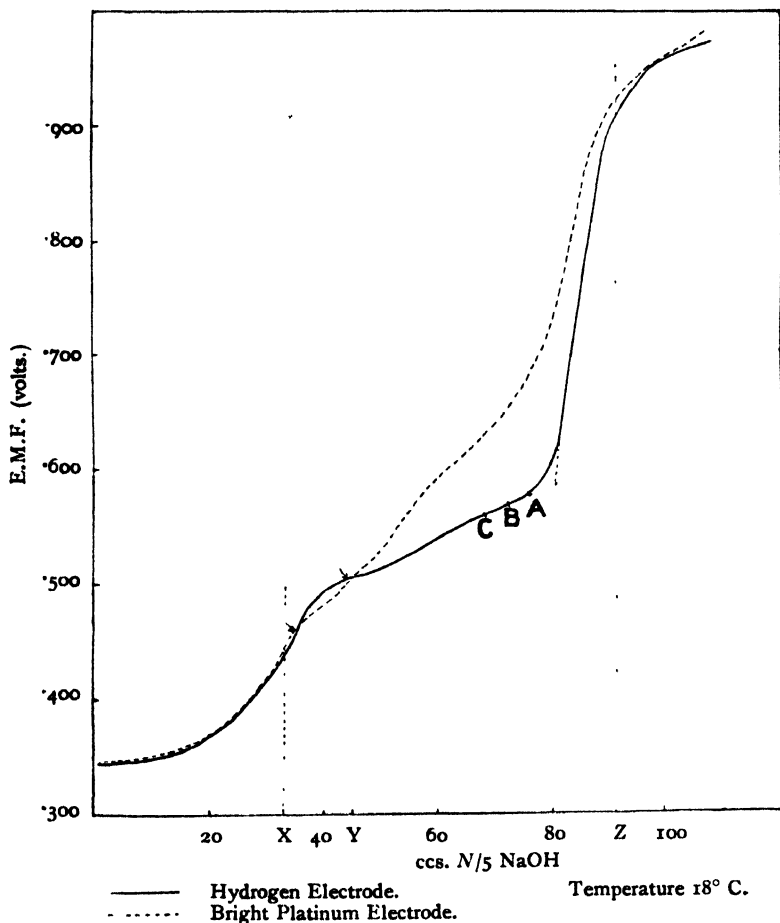


FIG. 1.

of the precipitation of $Cr(OH)_3$, agree approximately with the theoretical, but $Cr(OH)_3$ required much less than the theoretical amount of NaOH to complete the precipitation. This points to the precipitation of a basic sulphate. Britton⁹ notes the precipitation of basic sulphates by the action of dilute NaOH on many metallic salt solutions. Elder² states that this does not take place in the case of ferrous and ferric chloride solutions although Britton had previously obtained evidence of the precipitation of basic sulphates from both ferrous and ferric sulphate solutions.

Elder found that the hydrogen electrode functions as an oxidation-reduction electrode while appreciable amounts of ferrous and ferric ions are present together in solution, and the same effect is observed in this case with chromous-chromic solutions. The hydrogen electrode and the bright platinum electrode give very nearly the same readings until chromous hydroxide begins to be precipitated. It would appear that the potential of the hydrogen electrode in such solutions is governed by the $\text{Cr}^{2+}/\text{Cr}^{3+}$ potential until all the chromic hydroxide is precipitated and from thence forward, when the $[\text{Cr}^{3+}]$ is negligible in comparison with the $[\text{Cr}^{2+}]$ it is governed by the more rapidly adjusting $[\text{H}^+]$ of the solution. Elder² has calculated the solubility product of $\text{Fe}(\text{OH})_2$ using this argument, and this assumption applied to the above results gives a method of calculating an approximate value for $[\text{Cr}^{2+}][\text{OH}^-]^2$. Assuming that the hydrogen electrode is affected solely by the $[\text{H}^+]$ of the solution when all the chromic hydroxide is precipitated and the $\text{Cr}(\text{OH})_3$ is mostly precipitated, the p_{H} values at which $\text{Cr}(\text{OH})_3$ is precipitated at points A, B and C on the curve 4 c.c., 8 c.c. and 12 c.c. $N/5$ NaOH from the equivalence point are 5.59, 5.40 and 5.27 respectively. The equivalence point is obtained by producing the horizontal and vertical portions of the curve to meet each other. The assumption is made that the composition of the basic chromous hydroxide which separates is uniform over the precipitation range. Then the $[\text{Cr}^{2+}]$ at points A, B and C on the curve can be calculated from the volume of alkali which must be added at each point to attain the equivalence volume and the total volume of alkali required for the precipitation of $\text{Cr}(\text{OH})_3$. The $[\text{OH}^-]$ is calculated from the p_{H} , obtained from the *E.M.F.* of the hydrogen electrode, and K_w , which is taken as 0.73×10^{-14} at 18°C . From the curve the volume of $N/5$ alkali required to precipitate basic chromous hydroxide is seen to be 35.0 c.c. The following results were obtained :—

Cc. of NaOH Short of Equivalence Volume.	$[\text{Cr}^{2+}]$.	p_{H} .	p_{OH} .	$[\text{OH}^-]$.	$[\text{Cr}^{2+}][\text{OH}^-]^2$.
4 c.c.	2.64×10^{-3}	5.59	8.54	2.88×10^{-8}	2.20×10^{-20}
8 c.c.	5.40×10^{-3}	5.40	8.73	1.86×10^{-8}	1.88×10^{-20}
12 c.c.	8.30×10^{-3}	5.27	8.86	1.30×10^{-8}	1.67×10^{-20}

The solubility product of $\text{Cr}(\text{OH})_3$ can thus be taken as approximately 2.0×10^{-20} at 18°C . The p_{H} of precipitation of $\text{Cr}(\text{OH})_3$ from the above dilute solutions which may be taken as 5.6 is very close to the initial p_{H} of precipitation of $\text{Cr}(\text{OH})_3$ which is given by Britton as 5.3 and this would account to some extent for the badly-defined inflections in the titration curve.

The Calculation of Solubility Products from Titration Curves.

Britton⁹ obtained a number of curves for the titration of metallic salt solutions with alkali and calculated solubility products of the hydroxides from these, which, he stated, were in good agreement with values already obtained by other workers, although the precipitated hydroxides were often basic. Sweeney¹⁰ used Britton's data for the solubility product of $\text{Fe}(\text{OH})_2$ and recalculated the result. Elder²

¹⁰ Sweeney, *Trans. Amer. Elect. Soc.*, **53**, 324, 1928.

quotes Sweeney's figures, criticises Britton's method of calculation and suggests that the points on the curve from which the solubility product data were to be obtained, should be those recorded at the end of the titration when the $[\text{Fe}^{2+}]$ is relatively low and not at the beginning of the titration where Britton's figures were obtained. Elder thus obtained values for $[\text{Fe}^{2+}][\text{OH}^{-}]^2$ ranging from $2.3.9.7 \times 10^{-16}$.

It is evident also that the use of readings taken at the end of the titration will help to eliminate errors due to the hydroxide or basic oxide being first present in the colloidal state before actual precipitation takes place. Britton has since¹¹ calculated solubility products of $\text{Fe}(\text{OH})_2$ from data obtained over the entire range of precipitation and these vary progressively from 9×10^{-19} to 1×10^{-16} . He now states, arguing from this, a similar variation in the case of $\text{Pb}(\text{OH})_2$ and in a lesser degree $\text{Co}(\text{OH})_2$ that the solubility product principle is untenable in the case of the formation of basic precipitates generally, although it appears to hold in the precipitation of $\text{Ag}(\text{OH})_2$. This statement appears to be rather sweeping as even in the cases of the precipitation of $\text{Mg}(\text{OH})_2$, $\text{Mn}(\text{OH})_2$, $\text{Ni}(\text{OH})_2$, $\text{Cu}(\text{OH})_2$ and $\text{Al}(\text{OH})_3$ from sulphate solutions, where basic sulphates are undoubtedly formed, the solubility product calculated from the precipitation curve at the end of the precipitation is never more than ten times the value at the beginning of the titration, in spite of the fact that the system could hardly have reached equilibrium during the comparatively short period required for a titration.

It is significant that although Britton's values for $[\text{Fe}^{2+}][\text{OH}^{-}]^2$ vary so widely the value which he obtained at the end of the titration, *i.e.*, 1×10^{-16} is more consistent with other published values which range from 1.64×10^{-14} to 4.8×10^{-16} ,¹² excluding Britton's previously published values and Sweeney's recalculation of them, than the value of 9×10^{-19} obtained at the beginning.

Having regard to the above the solubility product of $\text{Cr}(\text{OH})_3$ was calculated from data obtained at the end of the titration and the product obtained is approximately constant.

Summary.

(1) Sulphuric acid solutions of chromous and chromic sulphates have been titrated with caustic soda, using the hydrogen and bright platinum electrodes as indicator electrodes. Inflections in the hydrogen electrode titration curve corresponding to the three stages of neutralisation of the alkali are obtained, but these are not sharp enough for quantitative purposes.

(2) The hydrogen electrode has been found to behave as an oxidation-reduction electrode governed by the $\text{Cr}^{2+}/\text{Cr}^{3+}$ equilibrium until $\text{Cr}(\text{OH})_3$ is completely precipitated, after which it behaves normally.

(3) The p_{H} of precipitation of $\text{Cr}(\text{OH})_3$ from very dilute solutions of CrSO_4 has been found to be 5.6 and from this the solubility product of $\text{Cr}(\text{OH})_3$ has been calculated.

The author wishes to express his thanks to Dr. H. J. S. Sand for his interest and advice during the course of this work.

*Sir John Cass Technical Institute,
London, E.C. 3.*

¹¹ H. T. S. Britton and R. A. Robinson, *Trans. Farad. Soc.*, **28**, 541, 1932.

¹² Randall and Frandsen, *J. Amer. Chem. Soc.*, **54**, 46, 1932.

STUDIES IN ADSORPTION.

PART I.—ADSORPTION OF CARBON DIOXIDE, SULPHUR DIOXIDE AND WATER.

By R. C. BOSWORTH (*University of Adelaide*).

Communicated by E. K. RIDEAL.

Received 25th October, 1932.

In 1927 M. L. Oliphant,¹ working in this laboratory, measured the number of CO₂ molecules adsorbed on mercury from excess of both hydrogen and argon. His results led to the conclusion that the adsorbed layer is monomolecular and that the film is practically complete when the gas phase contains 2 per cent. or more of carbon dioxide.

The method and apparatus employed in the present work is, with certain modifications, the same as that used by Oliphant and may briefly be described as follows: Pure mercury fell in fine drops (0.1 mm.) down a vertical cylindrical tube. At the centre of this tube the gaseous mixture was introduced and divided into two streams one issuing from the top, the other from the bottom. Thus the downward stream was enriched by liberation of the gas molecules adsorbed on the falling mercury, and the upwards stream correspondingly impoverished. The two streams were subsequently taken through the double tube of a Rayleigh refractometer capable of indicating a change in refractive index of 1 in 10⁷. This change in refractive index was measured by a compensating device and from its value the percentage composition of the gaseous streams could be deduced. The mercury passed by means of a syphon from the bottom of the adsorption tube to a lower vessel from which it was pumped back to a reservoir supplying the shower. Circulation of the gas under investigation was maintained by means of a Sprengel pump. An earthed metal shield placed around the shower-head which helped to prevent electrification of the drops, was found necessary in some of the investigations.

Method of Working.

Both before commencement, and at various intervals throughout these experiments, the apparatus was thoroughly washed in warm chromic acid mixture, steamed out until all acid had been removed, rinsed in distilled water and dried in a stream of warm dry air. The mercury, in the first place, was purified by the method described by Burdon,² and during the experiments was washed from time to time either in distilled water, or very dilute mercurous nitrate, followed by distilled water.

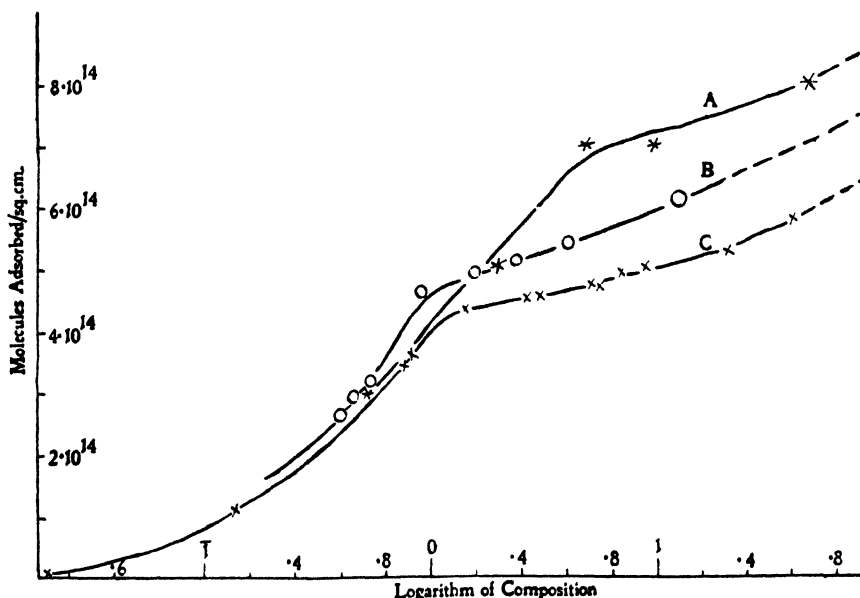
The gas mixtures, in the first place consisting of CO₂ and air, were admitted through a drying tube and circulated by means of the Sprengel

¹ Oliphant, *Phil. Mag.* (Ser. 7), 6, 422, 1928.

² Burdon, *Proc. Physic. Soc., Lond.*, 38, 148, 1926.

pump with the shower running until the interference fringes in the interferometer showed no further tendency to move. The shift of the fringes was then read and the composition of the gas deduced therefrom. From this and from a knowledge of the area of mercury surface falling per second, obtained by stroboscopically counting the drops and by measuring the weight of mercury which flows through the apparatus in unit time; together with a knowledge of the rate of flow of the gas; the adsorption per square centimeter could readily be computed. Measurements on sulphur dioxide were obtained in a precisely similar way. In all these determinations a drying tube containing glass wool soaked in strong sulphuric acid was included in the gas circuit.

In later experiments this drying tube was omitted and wet gases were used. Experiments on mixtures of air and carbon dioxide con-



A = CO_2 from dry hydrogen (Oliphant).
 B = SO_2 from dry air (Bosworth).
 C = CO_2 from dry air (Bosworth).

FIG. 1.

taining small amounts of water vapour indicated an adsorption which was definite but considerably less than that obtained with dry gases. This led to the use of a katharometer in series with the Rayleigh refractometer, enabling the variation in the composition of the two streams of gas with respect to two unknowns to be determined, and thus permitting a calculation of the number both of CO_2 and H_2O molecules adsorbed to be effected. Further experiments were carried out on mixtures of CO_2 and SO_2 and of SO_2 and H_2O .

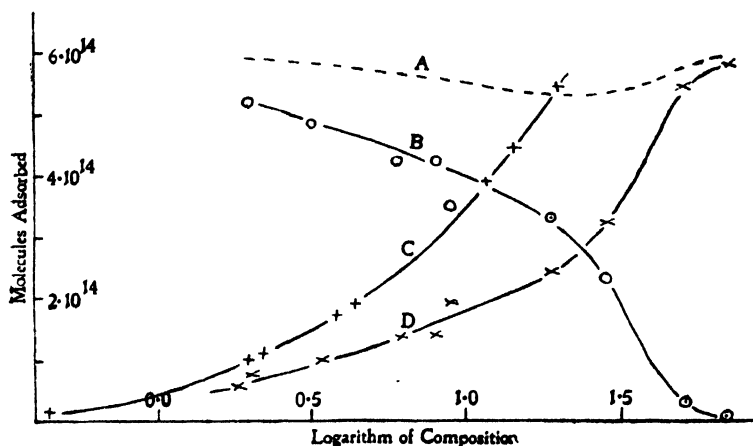
Results.

Let us represent the number of carbon dioxide molecules adsorbed on one square centimeter by N_{CO_2} , etc., and the percentage composition of the gas by C_{CO_2} , etc.

898 CARBON DIOXIDE, SULPHUR DIOXIDE AND WATER

The results for adsorption of CO_2 and SO_2 from dry air are shown on Fig. 1 where N_{CO_2} is plotted against $\log C_{\text{CO}_2}$ and N_{SO_2} against $\log C_{\text{SO}_2}$. Oliphant's points for CO_2 from dry hydrogen are added for comparison.

Figs. 2 and 3 gives the corresponding adsorption from moist air, the percentage of water vapour present being stated against each curve. The graphs for the total number of molecules adsorbed are shown as the dotted curves—these approximate to horizontal straight lines, *i.e.* the total number of adsorbed molecules appears to be independent of the relative concentrations of the constituents.



- A = Total number of molecules adsorbed $\text{CO}_2 + \text{H}_2\text{O}$.
 B = Number of H_2O molecules adsorbed (1.4 per cent. H_2O and varying amounts of CO_2).
 C = CO_2 from air containing 0.6 per cent. H_2O .
 D = CO_2 from air containing 1.2 per cent. H_2O .

FIG. 2.

The following results are not shown on the graphs : —

AIR, CARBON DIOXIDE, SULPHUR DIOXIDE MIXTURES.

C_{SO_2}	C_{CO_2}	$N_{\text{SO}_2} \cdot 10^{-14}$	$N_{\text{CO}_2} \cdot 10^{-14}$	$(N_{\text{CO}_2} + N_{\text{SO}_2}) \cdot 10^{-14}$
1.2	0.4	2.2	1.7	3.9
2.9	0.8	4.4	1.1	5.5
5.4	1.7	5.2	0.3	5.5

Water Vapour and Air.

$C_{\text{H}_2\text{O}}$	$C_{\text{H}_2\text{O}}$	$N_{\text{H}_2\text{O}} \cdot 10^{-14}$	$N_{\text{H}_2\text{O}}$
—	0.6	5	—

When working with saturated vapours no concordant results could be obtained, suggesting that the adsorption of a saturated vapour on an expanding mercury surface is quite an indefinite reaction. This

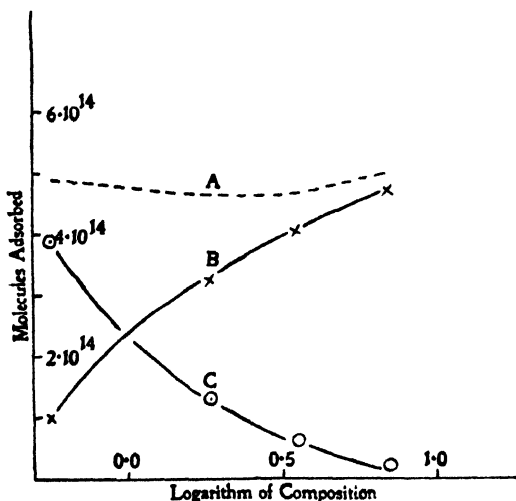
agrees with the conclusion of Iredale,³ that the surface tension of mercury is quite indefinite in the presence of a saturated vapour.

In the experiments on sulphur dioxide, there was strong evidence for the occurrence of some reaction other than pure physical adsorption

between the SO_2 and the expanding mercury surface, for on running the apparatus, all tubes through which mercury passed, became coated on the inside with a whitish deposit. This deposit appeared most copiously at places where the adsorbed molecules were liberated, *viz.*, at the bottom of the dropping chamber and of the Sprengel pump. On examination this film appeared to be composed mainly of amorphous sulphur. Further the mercury surface was affected in such a way that a drop of distilled water would spread rapidly across the surface of a sample

withdrawn from the apparatus. These observations lead to the conclusion that the mercury surface catalytically reduces part of the adsorbed SO_2 and permanently entrains some acidic or quasi-acidic reaction-product.

All of the experiments described in this paper were carried out in an underground room, the temperature variations of which fell within the limits 15.0°C. to 16.5°C.



A = Total number of molecules adsorbed $\text{SO}_2 + \text{H}_2\text{O}$.
 B = H_2O from air, 1.2 per cent. H_2O and varying amount of SO_2 .
 C = SO_2 from air containing 1.2 per cent. H_2O .

FIG. 3.

Discussion of Results.

Before commencing the experiments described in this paper, the instrument was set going with only dry air, freed from carbon dioxide, in the circulating system—no evidence of variation in composition was obtained. This must not be taken to imply that there is, for example, no selective adsorption of oxygen from nitrogen, since both the refractive indices and the thermal conductivities of these two gases are so nearly equal that the instruments used would only indicate large changes in oxygen or nitrogen content. It is known that oxygen is selectively adsorbed by such a metal as tungsten and Heyrovsky and Simunck⁴ also believe by mercury. These two authors used the hypothesis of an adsorbed oxygen layer to explain the Kucera anomalies in the electro-capillary curves for mercury. These Kucera anomalies

³ Iredale, *Phil. Mag.* (Ser. 6), 48, 177, 1924.

⁴ Heyrovsky, *Phil. Mag.* (Ser. 6), 45, 303, 1923; and Simunck, *ibid.* (Ser. 7), 7, 951, 1929.

consist in a discontinuous fall in the surface tension of a polarized mercury electrode, near the peak of the electro-capillary curve.

It may perhaps be said in criticism of these experiments that the mercury surface falling through the active gas does not remain in contact with it long enough for adsorption to be complete. For Popesco⁵ has determined the surface tension of mercury in contact with various gases, and, finding a progressive change in the surface tension extending over twenty-four hours or more, infers that the mercury slowly comes into adsorptive equilibrium with the gas. Mitton,⁶ on the other hand, has shown from kinetic principles that adsorptive equilibrium must be reached in less than $\frac{1}{100}$ second, a conclusion in accord with the theories of Langmuir. In the experiments just described, the drops of mercury are in contact with the gas for about $\frac{1}{4}$ second. This time

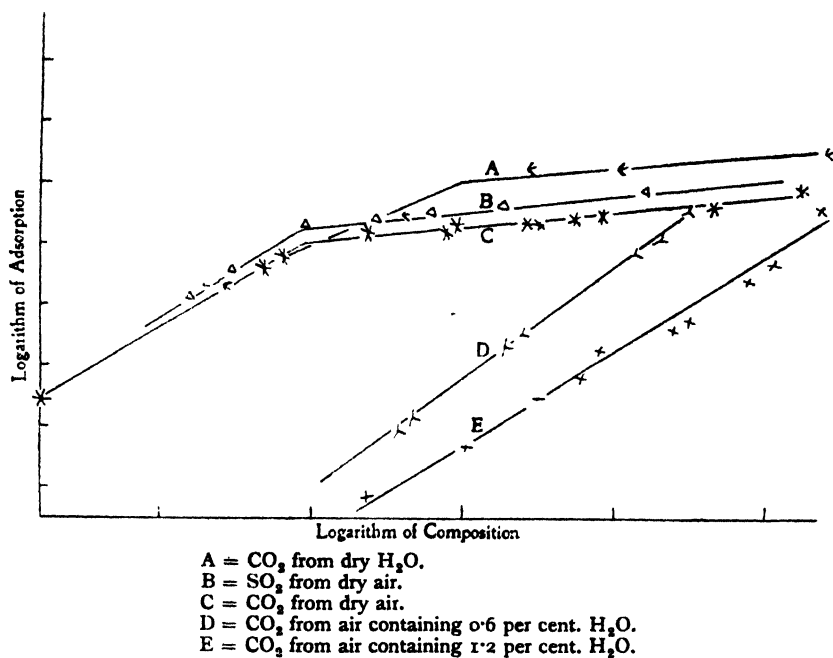


FIG. 4.

should be ample to allow for attainment of equilibrium in the adsorbed layer. As a matter of fact one would rather expect that the adsorption would be complete before the original random distribution of the mercury molecules at the newly formed surface could be destroyed by orientation. In other words, this method studies adsorption on a dynamic and not an equilibrium and oriented surface.

Calculation of the number of carbon dioxide molecules required to form one square centimeter of a monomolecular layer on the assumption that this layer has the same bulk density as liquid CO₂, shows that some 5.6×10^{14} molecules are required. Comparing this figure with the one found experimentally above shows that the gases studied give monomolecular layers which are close-packed when the air contains 1 per

⁵ Popesco, *Ann. Physique* (Ser. 10), 3, 4, 1925.

⁶ Mitton, *Trans. Roy. Soc. of S.A.*, 53, 267, 1929.

cent. or more of the capillary active gas. Where mixed gases are used the total layer is monomolecular and introducing more molecules of one type means displacing molecules of the other type, molecule for molecule, in a way which is reminiscent of the displacement type of chemical reaction.

Application of Gibbs's Equation.

The approximate form of this equation most useful when dealing with gases is

$$\Gamma = - \frac{1}{RT} \frac{d\sigma}{d \ln p}.$$

Where Γ is surface excess concentration,
 R the gas constant,
 T the absolute temperature,
 σ the surface tension,
 and p the partial pressure due to the active gas.

Expressing this equation in terms of molecular, not molar, quantities we get

$$n = - \frac{1}{RT} \frac{d\sigma}{d \ln p}.$$

Where k is the Boltzmann gas constant and n the number of molecules adsorbed, the integral form of the above equation is

$$\sigma_1 - \sigma_2 = 2.303 kT \int n d(\log p),$$

or, the decrease in surface tension below the dynamic value produced by CO_2 (or SO_2) should be equal to $2.303 kT$ multiplied by the area enclosed by the $n - \log c$ curve, the x axis and the ordinate $\log c = 2$.

Taking T as 287 we get

$$\begin{aligned} \sigma_1 - \sigma_2 &= 116 \text{ for } \text{CO}_2 \\ &= 136 \text{ for } \text{SO}_2. \end{aligned}$$

The second figure is possibly far too low, as the chemical reaction between the mercury and the sulphur dioxide can only mean that every N_{SO_2} is an underestimate.

The above figures may be compared with actual measured surface tension lowerings produced by CO_2 and SO_2 . Popesco's⁶ figures, for example, show that the difference between the values finally attained in CO_2 and the extrapolated value of a freshly formed drop is 130 dynes per centimetre and the corresponding figure for SO_2 is 213 dynes. Cook's⁷ determination of the surface tension lowering produced by CO_2 gave 88 dynes per centimetre.

Application of the Freundlich Isotherm.

This equation is given in the form

$$x/m = aC^{1/b}$$

Where x is the amount adsorbed,
 m the mass of the adsorbent,
 C the equilibrium concentration,
 and a and b are constants.

⁷ Cook, *Physic. Rev.* (Ser. 2), **34**, 513, 1929.

Applied to the case in hand it indicates a relationship of the type

$$n\alpha c^{1/b}$$

or a linear relationship between $\log n$ and $\log c$.

The results of plotting $\log n$ against $\log c$ are shown on Fig. 3. The curves for dry CO_2 and SO_2 consist of two linear sections. The lower linear portion of each of these curves has a slope $\left(\frac{d \log n}{d \log c} = \frac{1}{b}\right)$ of $\frac{1}{3}$ and at a point $\log c = 1$, i.e. for a gas containing 1 per cent. of either CO_2 or SO_2 this changes abruptly to a slope of only $\frac{1}{10}$. Oliphant's few figures (CO_2 from H_2) may be interpreted as giving a curve of the same general type with the point of discontinuity at a somewhat higher value of $\log c$. The values obtained for CO_2 adsorbed from moist air also gives straight lines whose slopes approximate to $\frac{1}{3}$, making it appear that, as long as the adsorbed layer is not saturated with molecules of the component under consideration (with dry gases the monomolecular layer was not complete below 1 per cent.), then the relation between the number of molecules of that given component in the adsorbed layer and the number of the same molecular type in the atmosphere above, is of the form: $n\alpha c^{\frac{1}{3}}$. This relation implies that the number of molecules of the given kind present on unit area on the mercury surface is proportional to the number in the sectional area of the gas above the mercury. The most obvious interpretation of this result would seem to be that we are here concerned with a two-dimensional type of Kinetic Equilibrium. No such type, however, appears to have been contemplated by theoretical workers on adsorption.

Summary.

Using a Rayleigh Refractometer to measure the small changes in composition produced when a shower of small drops of mercury falls through a column of mixed gas, it is found that :

(1) CO_2 , H_2O and SO_2 are all selectively adsorbed on the mercury surface.

(2) The layers are confined to monomolecular.

(3) The time taken for complete adsorption is certainly less than $\frac{1}{4}$ second.

(4) When the gaseous phase contains two active gases the adsorbed phase also contains these two components in relative proportions which increase with the relative concentrations.

(5) The total number of adsorbed molecules corresponds to a complete monomolecular layer and is independent of the relative concentrations of the active gases.

(6) For a layer not saturated with the given component the relation between n and c is $n\alpha c^{\frac{1}{3}}$.

In conclusion the author would like to express his sincere thanks to Professor Kerr Grant and to Mr. R. S. Burdon for the interest they have taken in this work, and for the many ways in which they have helped the author carry it out.

*Physics Department,
University of Adelaide,
5th September, 1932.*

STUDIES IN ADSORPTION.

PART II. ADSORPTION OF THE LOWER FATTY ACIDS.

Received 25th October, 1932.

By R. C. BOSWORTH.

Communicated by E. K. RIDEAL.

In Part I. the instrument used to measure the amount of gas adsorbed, *viz.*, the Rayleigh Refractometer, although perfectly satisfactory from the point of view of sensitivity, had the big drawback of rendering the apparatus extremely bulky and thus the duration of any one determination unduly lengthy. In the present paper there will be described a smaller and more static type of apparatus capable of measuring adsorption in one-sixth of the time.

The electrolytic conductivity of an aqueous solution is the property which has been used to provide a sensitive measure of small amounts of these acids.

In the first instance, it was thought that if a stream of water drops were formed in, and allowed to fall through air containing a definite amount of some acidic vapour, and then collected in a container connected to the bottom of the dropping-chamber, some evidence for the existence of a primary monomolecular film would be obtained. Air contained acetic and formic acid vapours was experimented with, and it was found that the amount of acid removed (as determined by the conductivity of the water formed by the coalescence of the drops) was roughly proportional to the partial pressure of the acidic vapour and exceeded the amount required to form a monomolecular layer many hundred-fold.

It appeared, therefore, that the drops remained in contact with the vapour long enough for considerable surface solution to take place.

It was then thought that mercury, a liquid in which these acids are insoluble might give more evidence for a true adsorptive phenomenon. Accordingly mercury was used instead of water.

Apparatus and Method.

The mercury from a constant level reservoir flowed down through constrictions limiting the rate of flow, to the dropper which consisted of a single orifice made by drawing down a piece of glass tubing to a fine capillary and then cutting off in the middle of the constriction. The tube leading to this dropper passed through a rubber cork which fitted into the top of the dropping chamber—a glass tube 20 cm. long by 7 cm. diameter. A side tube was sealed on to this dropping chamber somewhere near the centre, and was connected to the katharometer which was used to measure the fatty acid content of the air. Two other side tubes were used for drawing vapour into the dropping chamber, one being connected to a bubbler containing the liquid acid and the

other to a suction-pump. To the rounded bottom of the dropping chamber was sealed a short narrow piece of glass tubing, accurately aligned with the dropper so that drops fell out through this tube without touching the sides. This exit tube fitted into a cork in the neck of a small flask containing a weighted amount of conductivity water. The entire apparatus was made in Pyrex and cleaned in a like manner to the apparatus used in Part I. The mercury also was cleaned as before.

TABLE I.—ADSORPTION OF FORMIC ACID FROM DRY AIR.

Vapour Pressure (<i>p</i>), mm.	Adsorption $\times 10^{-14}$.
1.7	0.8
4.3	1.8
7.3	2.6
11.0	3.4
16.0	4.3
20.0	4.9
22.0	5.7
23.0	6.3
25.0	8.5
28.0	12
29.0	29
32 (Saturated)	126

In making a determination the exit tube was first corked and a few cubic centimetres of vapour drawn into the dropping chamber. After waiting until the katharometer reading was steady the cork was removed, the collecting flask placed in position and the mercury drops turned on. After collecting for a definite time (during which time the katharometer was read at intervals) the mercury drops were turned off and the flask removed and weighed in order to measure the volume of mercury collected. The water was decanted

into a conductivity cell and its content of fatty acid determined. The only other factor required in order to obtain the number of molecules adsorbed per square centimetre is the rate of dropping or number of drops formed in unit time. To measure this a neon lamp stroboscope was found most convenient. This consisted in an ordinary neon lamp from which the stabilising resistance was removed. The lamp was connected in parallel with a $0.1 \mu\text{F}$ fixed condenser and in series with a high resistance. For this high resistance an ordinary triode valve was used, its anode-filament impedance, forming the high resistance, which could be varied by varying the filament current. When this arrangement was connected to the 200 D.C. supply, negative to the filament and positive through the lamp and condenser to the plate, the lamp was set flashing. The lamp was placed behind the dropper and the flashes were synchronised with the rate of dropping. A mechanical relay was placed in series with the neon tube, and in its secondary circuit was a "Cenco" impulse counter which thus recorded the number of drops. A rate of dropping of some 8-12 drops per second was found to give the most regular stream and accordingly such a rate was adhered to in all these experiments.

TABLE II.—ADSORPTION OF FORMIC ACID DILUTED WITH LABORATORY AIR.

<i>p</i> , mm.	$\times 10^{-14}$.
4.0	0.8
11.0	1.1
12.0	1.2

Results.

The results obtained with the apparatus as just described seemed at first to indicate that the adsorption on mercury was exactly the

same as that on water. But it is obvious that the air in the dropping chamber must be saturated with water vapour, and it has already been shown that a saturated vapour gives a multimolecular layer on mercury. Now it has been shown (Part I.) that the water surface of a true adsorbed or monomolecular layer has no adsorptive properties of its own, but there is no reason for believing that the surface molecules of a multimolecular or condensation layer of water will have properties other than those of water molecules on an ordinary water surface, for they are under the control of the valency fields of the water molecules immediately beneath and far beyond the field of the mercury surface. Thus we are led to believe that the mercury drops formed in saturated air are covered with a condensation layer of water molecules and that this water layer is

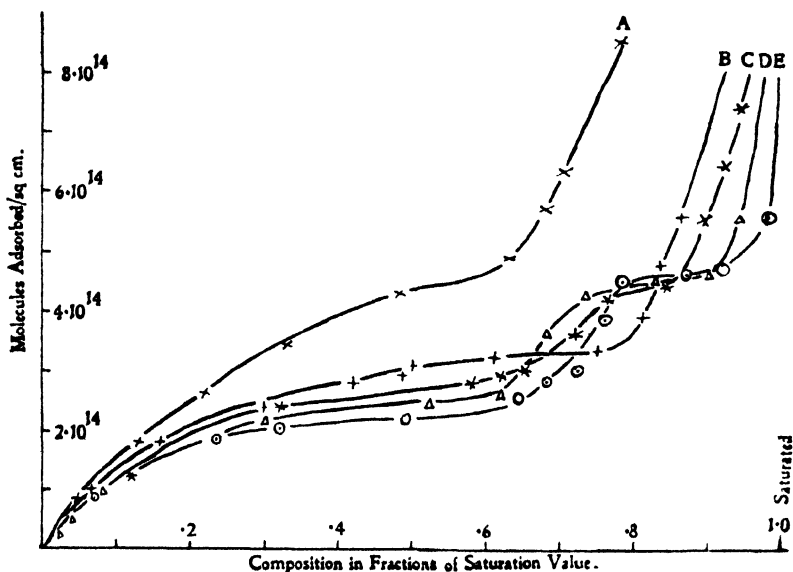


FIG. 1.

- A = Formic acid.
- B = Acetic acid.
- C = Propionic acid.
- D = Butyric acid.
- E = Valeric acid.

capable of dissolving fatty acid in the same way as the surface of a water drop. In order, therefore, to get a pure mercury surface, it was necessary to remove this water vapour. The dropping chamber was dried in a stream of warm dry air for three days and afterwards only air which had been previously dried over sulphuric acid was admitted to the apparatus. The collecting vessel, containing the weighted amount of water, was in all succeeding determinations placed below the dropping chamber with its neck no closer to the exit tube than 4 cm.

Using this dry apparatus the adsorption (n) of the first five fatty acids was determined at varying partial pressures (p) up to saturation. The results are given in tables I., II. and III.

A few results (given in Table II.) were obtained with the formic acid diluted with ordinary laboratory air. The adsorption was much smaller.

This would appear to indicate that moisture insufficient to form a condensation layer appears to act with formic acid as it did with CO_2 and SO_2 , viz., displace it from the adsorbed layer.

TABLE III.—ADSORPTION FROM DRY AIR.

<i>Acetic Acid.</i>		<i>Propionic Acid.</i>	
<i>p.</i>	$n \times 10 - 14.$	<i>p.</i>	$n \times 10 - 14.$
mm.		mm.	
1.0	0.9	0.4	1.2
2.7	1.8	0.7	1.4
3.5	2.3	1.0	2.4
5.0	2.8	1.7	2.8
5.7	2.9	1.9	2.9
5.8	3.1	2.0	3.0
7.1	3.2	2.1	3.6
8.8	3.3	2.2	4.2
9.5	3.9	2.3	4.3
10.0	5.6	2.6	5.6
11.0	23	2.7	6.4
11.6 (Saturated)	93-126	2.8	7.4
		2.9	19
		3.0 (Saturated)	91
<i>n-Butyric Acid.</i>		<i>a-Valeric Acid.</i>	
<i>p.</i>	$n \times 10 - 14.$	<i>p.</i>	$n \times 10 - 14.$
mm.		mm.	
0.01	0.2	0.02	0.8
0.04	0.8	0.07	1.9
0.05	1.0	0.09	2.0
0.07	1.1	0.13	2.2
0.22	2.2	0.18	2.6
0.39	2.5	0.19	2.8
0.48	2.6	0.20	3.0
0.50	3.6	0.21	3.9
0.57	4.3	0.22	4.5
0.66	4.5	0.25	4.6
0.68	4.6	0.27	4.7
0.71	5.6	0.29	5.6
0.75 (Saturated)	15-120	0.30 (Saturated)	14-120

These results are represented on Fig. 1 in which the adsorption (n) as ordinate has been plotted against the partial pressure expressed as a fraction of the saturation value as abscissa. It is seen that in all cases, as the partial pressure approaches the saturation value the adsorption changes abruptly from monomolecular to multimolecular, i.e., at, or near saturation the acid condenses on the mercury. Formic acid appears to give rise to these condensation layers most readily and the rest less and less readily as the size of the molecule increases. The curves for formic and acetic acids show n increasing steadily with p , but for the other three acids show an abrupt change at a certain p from one value of n to another much larger value. The natural interpretation of these results is that these acids are capable of existing on the mercury surface in different two-dimensional phases, one at low pressures and one at high, and that the passage from one phase to the other is com-

paratively sharp. On the other hand formic and acetic acids appear to be capable of existing in one two-dimensional phase only.

If we take the limiting value of n as defining the area (a) occupied by one molecule on the surface, by

$$a = 1/n,$$

it follows that formic acid occupies an area of 23 square Angstroms per molecule, acetic acid 31 Å², propionic acid 36 Å² or 22 Å², butyric acid 40 Å² or 22 Å² and valeric acid either 45 Å² or 22 Å², showing that in the high pressure phase the area occupied per molecule is independent of the length of the carbon chain and identical with the area occupied by formic acid, *i.e.*, that area of the carboxyl group; and in the low pressure phase the area per molecule increases regularly with the length of the carbon chain.

An explanation of this behaviour may be given in terms of orientation of the molecules.

It is known from the work of Von Szyszkowski¹ and others on the effect of the lower fatty acids on water that these acids give gaseous films in which the fatty acid molecules are lying flat on the water surface. Again the work of Langmuir² has shown that the higher insoluble fatty acids give films in which the area occupied per molecule is independent of the length of the carbon chain, this is interpreted as meaning that these acids are oriented on their carboxyl

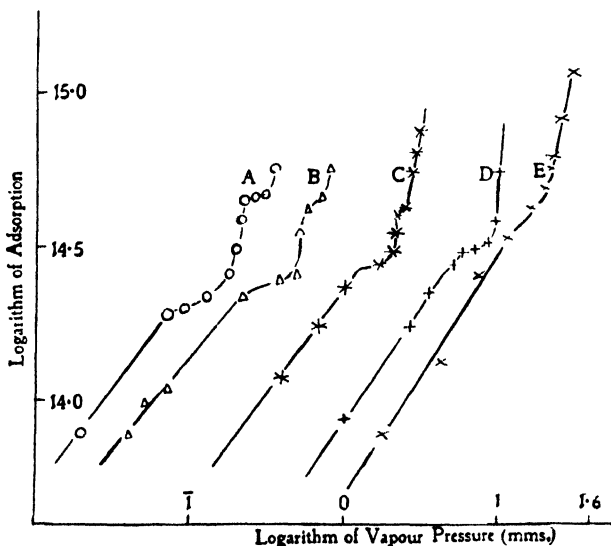


FIG. 2.

- A = Valeric acid.
- B = Butyric acid.
- C = Propionic acid.
- D = Acetic acid.
- E = Formic acid.

groups and the area occupied per molecule (22 Å²) is the area occupied by the end or carboxyl group. These acid films are closely packed solid or liquid two-dimensional phases. With acids of intermediate molecular weight such as tridecylic or myristic it is possible to compress the films from the expanded to the condensed state. With surface films on mercury this transitional stage appears to be attained with much lighter molecules, for propionic, butyric and valeric acids give films which are capable of being compressed from the gaseous to the condensed and oriented state by increasing the two-dimensional pressure

¹ Von Szyszkowski, *Z. physik. Chem.*, **64**, 385, 1908.

² Langmuir, *J. Amer. C.S.*, **39**, 1848, 1917.

on the film, *i.e.*, increasing the partial pressure of the acidic vapour in bulk phase. On the other hand formic and acetic acids give films which are always gaseous.

In the low pressure phase referred to above it therefore appears that the fatty acid molecules are lying flat on the surface and the regular increase of area with length of carbon chain is at once explained—each additional CH_2 group adds 5 \AA^2 to the area occupied by the molecule. In the high pressure phase the molecules are oriented on their active ends or carboxyl groups and accordingly occupy the same area per molecule as formic acid which is virtually no more than a carboxyl group.

The Two-thirds Power Law.

Fig. 2 shows $\log n$ plotted against $\log p$ and shows that the relation between n and p over the range of p for which the film is not tightly packed, is of the form $nap^{\frac{2}{3}}$.

Determination of Adsorption by Means of Surface Tension Measurements.

An attempt was made to verify the above results by some independent method, and the drop-weight method of measuring surface tension was chosen. The apparatus used was similar to that used by Iredale,³ the only important difference being that the composition of the vapour used was, as above, measured by means of a katharometer—the assumption being made that over the small range of composition used the deflections of this instrument were proportional to the composition.

The diameter of the jet used was 0.1551 cm. and the formula used to calculate surface tension from the drop weight was that given by Harkins and Brown,⁴ *viz.* :

$$W = 2\pi r \sigma f(r/v^{\frac{1}{3}}).$$

Where

W is the drop weight,
 r the radius of the tube,
 σ the surface tension,
 f the function given by Harkins and Brown,
 and v the volume of the drop.

The correcting factor $f(r/v^{\frac{1}{3}})$ came out to be 0.605 so that the formula used was

$$W = 3.8r\sigma,$$

i.e., identical with that given by Rayleigh.

At the beginning of the determinations the effect of the rate of dropping on the drop weight was obtained, and it was found that as long as the time of drop formation exceeded ten seconds the weight of the drop was independent of the time taken in its formation. A rate of dropping of six a minute has accordingly been adopted throughout the rest of this work.

The mercury used was of the same high grade as used in other experiments on surface tension in this laboratory.

³ Iredale, *Phil. Mag.* (Ser. 6), **45**, 1095, 1923.

⁴ Harkins and Brown, *J. Amer. C.S.*, **41**, 511, 1919.

Determination of the surface tension of mercury in air at 14° C. led to the result

$$\sigma = 482 \text{ dynes per centimetre,}$$

a figure not affected by drying out the apparatus.

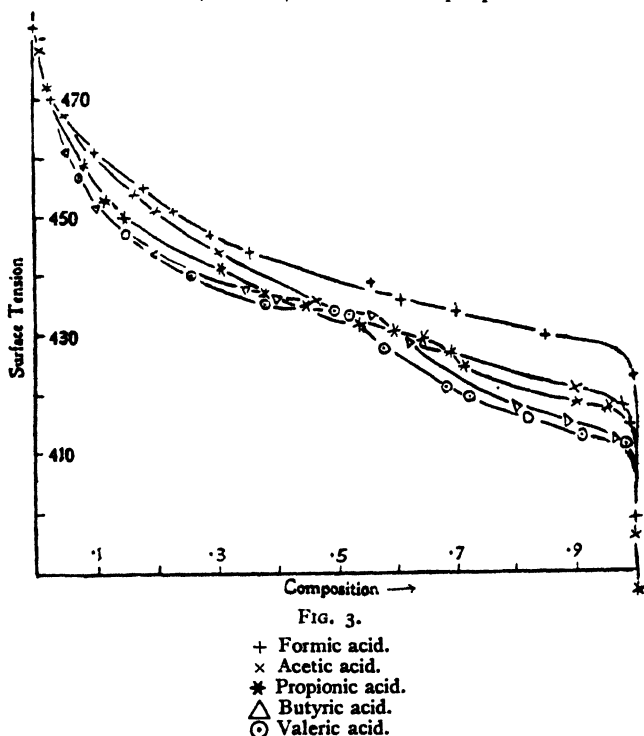
Traces of butyric acid vapour were then added, the composition read on the katharometer and the drop weight taken. More acid vapour was added and the observations repeated till the vessel was saturated with butyric acid. The vapour was then removed bit by bit until the mercury came back to its original drop weight—it was frequently found necessary to heat the glass to redness and evacuate before the last traces of these acids could be removed. Following butyric the other four acids were used in the order: valeric, acetic, formic and propionic. The results are shown on Fig. 3 in which surface tensions are plotted against compositions expressed as fractions of the saturation concentration.

The curves show that formic acid produces the least effect on the surface tension of mercury, the rest following in order of molecular weight. Thus the surface tension lowering produced is in the inverse ratio of the surface tension of the pure acids—formic acid has the highest surface tension and valeric the lowest.

The curves for formic and acetic acids are smooth but for butyric and valeric acids a marked discontinuity occurs at about $p = 0.6$ saturated—thus confirming the discontinuities found by the adsorption measurements. With propionic acid the discontinuity appears much less marked but is definitely present.

In all cases saturation leads to a discontinuous drop in the surface tension to less than 400 dynes per centimetre. This change is much more abrupt and occurs at higher partial pressures than the corresponding change from mono- to multimolecular adsorption.

Possibly the fast rate of dropping in the adsorption experiment would lead to a cooling of the drops as they formed with resultant



local supersaturation and the formation of multimolecular layers. On the other hand the slowly forming drop in the drop-weight experiment keeps in thermal equilibrium with its surroundings.

Comparison of these Two Sets of Results with the Aid of Gibb's Equation.

A comparison of measured surface tension changes with the values calculated from the adsorption curves by the method used in the previous paper, shows that the measured values are in all cases much larger than the calculated. Now the accuracy with which $\{nd \log p$ is evaluated is determined largely by the accuracy with which n is measured when p is small. Evidence will be produced later to show that just these particular readings are seriously in question. It is accordingly more instructive to calculate n from the σ - p curve and compare such values of n with the ones measured independently.

Gibbs' equation is written in the form used before, *viz.*,

$$n = - \frac{1}{kT} \frac{d\sigma}{d \log p}$$

$$= 1.1 \times 10^{13} \frac{d\sigma}{d \log p},$$

$\frac{d\sigma}{d \log p}$ is obtained by drawing the $\sigma - \log p$ curve and measuring the slope at various points.

Table IV. compares the calculated with the observed values of n .

TABLE IV.

Acid.	p .	Calculated $n \times 10^{-14}$.	Observed $n \times 10^{-14}$.
Formic	1.7 mm.	2.0	0.8
	3.4	2.4	1.4
	7.0	2.6	2.5
	14.0	4.1	4.1
	18.5	4.6	4.7
Acetic	0.6	2.3	0.7
	1.3	2.6	1.2
	4.0	3.0	2.5
	6.6	4.0	3.0
	9.7	4.5	4.0
Propionic	0.3	2.6	1.0
	1.6	2.8	2.5
	2.5	4.4	4.4
Butyric	0.08	2.6	1.2
	0.32	2.6	2.4
	0.64	4.9	4.5
Valeric	0.03	2.2	1.0
	0.13	2.3	2.2
	0.26	5.2	4.6

This table shows that for all values of p greater than about 0.30 saturated theory agrees with experiment about as well as could be expected; but for p less than 30 per cent. saturated the calculated values of n are far too high, the discrepancy being the worse the smaller p . It would appear, therefore, that there is some cause producing abnormally

low adsorption at low partial pressures. Two possible sources of error suggest themselves at once.

(1) The mercury drops fell through 4 cm. of air before reaching the flask in which they were collected. If the "time of relaxation" or the average life of a molecule in the adsorbed layer is small in comparison with a second, there will be very considerable evaporation from the adsorbed layer while the drop is falling through air. If this had been the cause of the low values it is to be expected that all values measured by this apparatus would have been uniformly too small—but this is not so, the values obtained with higher values of p agree with theory. And so we turn to the alternative hypothesis.

(2) There is some impurity present which is being adsorbed at low pressures, preferentially to the fatty acid, and so is displacing the acid molecules from the adsorbed layer. One does not need to look far for this impurity—water vapour is undoubtedly present in the dropping chamber as a result of diffusion from the water in the collecting flask. Now it was shown when working with CO_2 that water vapour displaces CO_2 from the adsorbed layer, but when great excess of CO_2 was added the water could be completely driven out of the adsorbed layer. There is every reason for believing that the fatty acids would act in the same way. The few results quoted under formic acid show that deliberately increasing the amount of water vapour, still further represses the adsorption. Accordingly it appears that the low values of n at low p are the result of the presence of water vapour. This view receives further support from the two-thirds power relationship mentioned above. This law is in direct contradiction to the theory of Langmuir,⁵ where he shows that, at low pressures the relationship between n and p to be expected, is of the form $n \propto p$.

In the development of this relationship Langmuir assumed strict reversibility of the adsorption process. Now it is obvious that in the cases studied above the adsorption is not reversible—the rate of desorption when passing through air is not as large as the rate of adsorption. Moreover, evidence appears to show that the two-thirds power law is a law governing adsorptive displacement rather than a law of adsorption. The law is most prominent when dealing with moist gases, and it is not unreasonable to believe that with the so-called dry gases the appearance of this law below a certain p was due to the fact that the gases were not quite dry. Thus we may attribute the relationship between n and p for the fatty acids to the fact that over this range for which this relationship holds the fatty acids are being displaced from the adsorbed layer by water vapour. This view is further supported by the fact that it is just over this range the divergences from Gibbs' equation appear.

Summary.

Using a conductivity cell in place of the Refractometer the adsorption on mercury from the vapour phase of the first five fatty acids has been measured.

(1) The layers are monomolecular provided the vapours are not saturated or nearly saturated—multimolecular when they are saturated.

(2) Propionic, butyric and valeric acids appear to be capable of forming two types of adsorbed layers—acetic and formic acids only one.

⁵ Langmuir, *J. Amer. C.S.*, 40, 1361, 1918.

(3) These results are confirmed by drop-weight measurements of the surface tension.

(4) Comparison of the two sets of results gives confirmation of Gibb's equation when the concentrations are over 30 per cent. saturated, but complete disagreement at low concentrations.

(5) A reason for this disagreement is advanced.

In conclusion the author would like to express his sincere thanks to Professor Kerr Grant and to Mr. R. S. Burdon for the interest they have taken in this work, and for the many ways in which they have helped the author carry it out.

*Physics Department,
University of Adelaide,
5th September, 1932.*

A STUDY OF THE SYSTEM WATER-PHENOL. PART II. VISCOSITIES.

BY OWEN RHYS HOWELL.

Received 13th October, 1932.

(Communicated by Eric K. Rideal.)

The solutions used in this investigation were the same as those employed for the density determinations which have been the subject of a previous communication.¹

The viscosity coefficients were determined in viscometers of the Ostwald type, made of Pyrex and specially designed to prevent change in concentration of the solutions by evaporation. The apparatus and the method of cleaning and of use have already been described.² The dimensions of the viscometers were in accordance with the recommendations of Applebey³ and Washburn and Williams⁴ and no kinetic energy correction has been applied. In none of the determinations was there any turbulent flow; the Reynolds number⁵ was never greater than 250.

The values of the viscosity coefficient for water used in these determinations are those of Bingham and White⁶ except for 60°, where the quoted value is evidently too high and the smoothed value of 0.004700 is accepted.

Viscosity-concentration Relation.

The viscosity coefficients observed at all concentrations at each temperature are collected in Table I. and plotted in Fig. 1. The values

¹ *Roy. Soc. Proc.*, **137**, 418, 1932. The melting-point of pure phenol recorded in this paper (p. 418) is misprinted. The figure $40.85^\circ \pm 0.50^\circ$ should read $40.85^\circ \pm 0.05^\circ$.

² Howell, *J. Chem. Soc.*, 158, 1927.

³ *J. Chem. Soc.*, **97**, 2000, 1910.

⁴ *J. Amer. Chem. Soc.*, **35**, 737, 1913; see also Jones and Veazey, *Z. physik. Chem.*, **61**, 641, 1905.

⁵ Reynolds, *Phil. Trans., A.*, **174**, 935, 1883; **177**, 171, 1886.

⁶ *Z. physik. Chem.*, **80**, 670, 1912.

for the conjugate solutions are also shown in the figure and the boundary curve drawn through them.

TABLE I.

Conc. Phenol. Per Cent.	Viscosity Coefficient η_{sp} .											
	20°.		30°.		40°.		50°.		60°.		70°.	
	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
0	0.01006	0.01006	0.007998	0.007998	0.006563	0.006556	0.005500	0.005500	0.004700	0.004699	0.004075	0.004075
2	0.01036	0.01036	0.008342	0.008351	0.006816	0.006811	0.005696	0.005691	0.004850	0.004847	0.004190	0.004189
4	0.01107	0.01107	0.008703	0.008710	0.007085	0.007076	0.005898	0.005893	0.005000	0.005000	0.004310	0.004310
6	0.01160	0.01160	0.009071	0.009096	0.007370	0.007364	0.006110	0.006114	0.005188	0.005176	0.004450	0.004450
8	0.01215	0.01215	0.009485	0.009490	0.007664	0.007664	0.006340	0.006347	0.005360	0.005360	0.004600	0.004601
10							0.006600	0.006600	0.005568	0.005567	0.004771	0.004771
15									0.006261			
20											0.005954	
30											0.007590	
40											0.008925	
50											0.009729	
60									0.01293	0.01053		
70		(0.04080)	0.02972	0.02972	0.02253	0.02253	0.01775	0.01763	0.01413	0.01414	0.01157	0.01157
75	0.04372	0.04372	0.03153	0.03157	0.02381	0.02383	0.01858	0.01857	0.01485	0.01486	0.01215	0.01215
80	0.04731	0.04731	0.03393	0.03395	0.02553	0.02553	0.01981	0.01986	0.01591	0.01588	0.01298	0.01298
85	0.05273	0.05273	0.03742	0.03742	0.02792	0.02792	0.02164	0.02164	0.01725	0.01725	0.01405	0.01405
90	0.06146	0.06146	0.04288	0.04289	0.03161	0.03158	0.02420	0.02420	0.01910	0.01912	0.01547	0.01548
95		(0.07865)	0.05284	0.05284	0.03770	0.03775	0.02820	0.02820	0.02180	0.02181	0.01735	0.01734
100							0.03491	0.03491	0.02614	0.02618	0.02028	0.02028

The general form of the figure is very similar to that for the densities.¹ There is no obvious continuity between the portions of the curves for the water-rich and phenol-rich solutions below the critical solution temperature. The continuous curve for 70° is very complex, being first convex, then concave and again convex to the axis of concentration. No equation has been found relating viscosity and concentration.

Graham⁷ was the first to express the view that a maximum on the viscosity curve of binary mixtures indicated the existence and established the composition of a compound, and this has been shown to be true for a large number of pairs of substances by many different workers.⁸ Although this view is no longer accepted as being generally true, many observers hold that a maximum on the viscosity curve must be attributed to the formation of a compound, possibly in a state of partial dissociation.⁹

Thus, Dunstan and Thole¹⁰ state that "Based on the view that associated liquids in general and hydroxylated liquids in particular have a relatively high viscosity coefficient, the conclusion may be drawn that a maximum point in a viscosity-concentration curve means further association proceeding in the direction of complex formation, whilst the existence of a minimum point tends to the opposite view, namely, that some dissociation has resulted." In the present instance the two liquids are hydroxylated and are known to become further associated in that they form a definite hemi-hydrate, whilst the existence of association in equimolecular proportions has also been demonstrated, yet the curve, so far from showing a maximum, is sagged in

⁷ *Phil. Trans., A.*, 181, 373, 1861.

⁸ See Hatschek, *The Viscosity of Liquids*, p. 147, London, 1928.

⁹ Tsakalotos, *Bull. Soc. Chim.*, 3, 234, 1908.

¹⁰ *The Viscosity of Liquids*, p. 44, London, 1914.

this region. There is to be borne in mind, however, one consideration which does not seem to have been appreciated, namely, that the actual association on the formation of a hydrate or other compound may actually be less than that existing in one or both of the liquids.

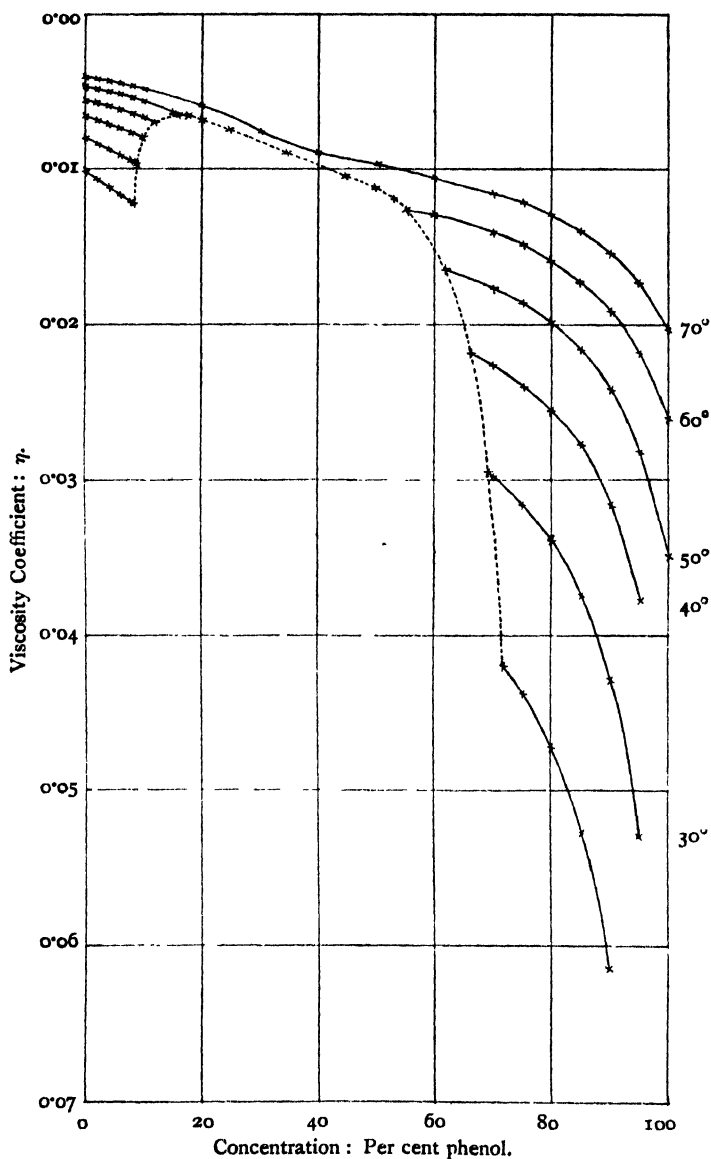


FIG. 1.

Jones and Veazey¹¹ assume that in a mixture of associated liquids the effect of each component is to reduce the association of the other, resulting in the formation of a large number of simpler aggregates, so

¹¹ *Amer. Chem. J.*, **37**, 405, 1907.

that the frictional surface is increased and the viscosity rises. This theory has not been favourably received, since instances are already known of pairs of associated liquids, for example, water-ethylene glycol,¹² where the viscosity curve shows no maximum but, on the contrary, is sagged. The water-phenol system affords a similar example.

It has, however, been pointed out by Findlay,¹³ and subsequently by many others, notably Denison,¹⁴ that it is not the maximum on the viscosity-concentration curve but the maximum deviation from the "ideal" mixture curve which affords the more reliable information. The ideal mixture law is, however, unknown and, therefore, as Hatschek⁶ has pointed out, the true deviation is not obtainable by assuming a linear law as is usually done. Nevertheless, interesting information can be obtained in this way.

In Table II. are given the values for 70° of the viscosity coefficients and also, for comparison, the densities calculated from the linear relation, the observed values and the differences. The differences are plotted against the concentration in Fig. 2.

TABLE II.

Conc. Phenol. Per Cent.	Density $d_{4}^{70^{\circ}}$.			Viscosity Coefficient $\eta_{70^{\circ}}$.		
	Ideal.	Obs.	Diff.	Ideal.	Obs.	Diff.
0	0.9778	0.9778	0	0.004075	0.004075	0
10	0.9833	0.9829	0.0004	0.005696	0.004771	0.000925
20	0.9887	0.9872	0.0015	0.007316	0.005954	0.001362
30	0.9942	0.9917	0.0025	0.008937	0.007590	0.001347
40	0.9997	0.9962	0.0035	0.010557	0.008925	0.001632
50	1.0052	1.0009	0.0043	0.012178	0.009729	0.002449
60	1.0106	1.0054	0.0052	0.01380	0.01053	0.00327
70	1.0161	1.0105	0.0056	0.01542	0.01157	0.00385
75	1.0188	1.0132	0.0056	0.01623	0.01215	0.00408
80	1.0216	1.0161	0.0055	0.01704	0.01298	0.00406
85	1.0243	1.0193	0.0050	0.01785	0.01405	0.00380
90	1.0270	1.0232	0.0038	0.01866	0.01547	0.00319
95	1.0298	1.0276	0.0022	0.01947	0.01735	0.00212
100	1.0325	1.0325	0	0.02028	0.02028	0

It is seen that for both properties, the curve shows a very well-defined maximum which, however, does not correspond to the hemihydrate or to equimolecular proportions of the two constituents. The position of the maximum varies with temperature; it is at about 77 per cent. at 70°, 78.5 per cent. at 60° and 80 per cent. at 50°. It is unfortunately impossible to follow the change further, since phenol ceases to be liquid at the next working temperature, but these values suffice to indicate that the maximum corresponds to a compound of equimolecular proportions of water and phenol, and that this is partially dissociated at these temperatures. The lower the temperature, the smaller is the dissociation and the nearer is the position of the maximum to the concentration corresponding to the compound.

¹² Dunstan and Thole, *J. Chem. Soc.*, **95**, 1556, 1909.

¹³ *Z. physik. Chem.*, **69**, 203, 1909.

¹⁴ *Trans. Farad. Soc.*, **8**, 20, 1912.

this region. There is to be borne in mind, however, one consideration which does not seem to have been appreciated, namely, that the actual association on the formation of a hydrate or other compound may actually be less than that existing in one or both of the liquids.

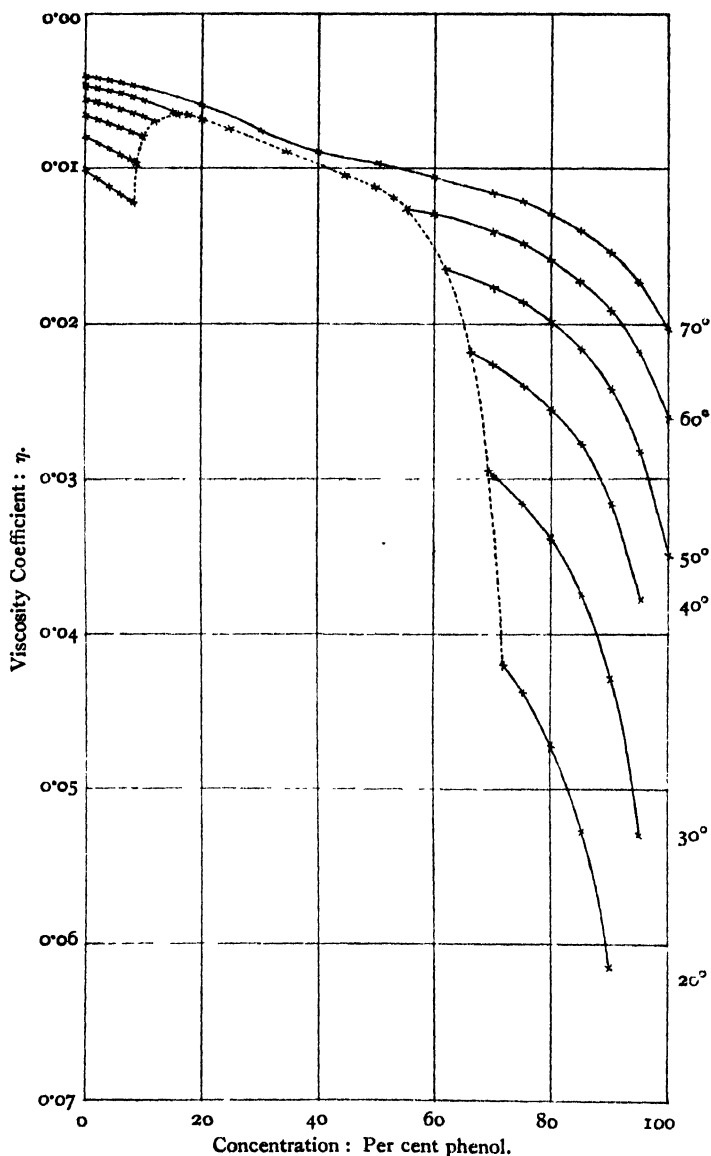


FIG. 1.

Jones and Veazey¹¹ assume that in a mixture of associated liquids the effect of each component is to reduce the association of the other, resulting in the formation of a large number of simpler aggregates, so

¹¹ *Amer. Chem. J.*, **37**, 405, 1907.

that the frictional surface is increased and the viscosity rises. This theory has not been favourably received, since instances are already known of pairs of associated liquids, for example, water-ethylene glycol,¹² where the viscosity curve shows no maximum but, on the contrary, is sagged. The water-phenol system affords a similar example.

It has, however, been pointed out by Findlay,¹³ and subsequently by many others, notably Denison,¹⁴ that it is not the maximum on the viscosity-concentration curve but the maximum deviation from the "ideal" mixture curve which affords the more reliable information. The ideal mixture law is, however, unknown and, therefore, as Hatschek⁸ has pointed out, the true deviation is not obtainable by assuming a linear law as is usually done. Nevertheless, interesting information can be obtained in this way.

In Table II. are given the values for 70° of the viscosity coefficients and also, for comparison, the densities calculated from the linear relation, the observed values and the differences. The differences are plotted against the concentration in Fig. 2.

TABLE II.

Conc. Phenol. Per Cent.	Density $d_{4}^{70^{\circ}}$.			Viscosity Coefficient $\eta_{70^{\circ}}$.		
	Ideal.	Obs.	Diff.	Ideal.	Obs.	Diff.
0	0.9778	0.9778	0	0.004075	0.004075	0
10	0.9833	0.9829	0.0004	0.005696	0.004771	0.000925
20	0.9887	0.9872	0.0015	0.007316	0.005954	0.001362
30	0.9942	0.9917	0.0025	0.008937	0.007590	0.001347
40	0.9997	0.9962	0.0035	0.010557	0.008925	0.001632
50	1.0052	1.0009	0.0043	0.012178	0.009729	0.002449
60	1.0106	1.0054	0.0052	0.01380	0.01053	0.00327
70	1.0161	1.0105	0.0056	0.01542	0.01157	0.00385
75	1.0188	1.0132	0.0056	0.01623	0.01215	0.00408
80	1.0216	1.0161	0.0055	0.01704	0.01298	0.00406
85	1.0243	1.0193	0.0050	0.01785	0.01405	0.00380
90	1.0270	1.0232	0.0038	0.01866	0.01547	0.00319
95	1.0298	1.0276	0.0022	0.01947	0.01735	0.00212
100	1.0325	1.0325	0	0.02028	0.02028	0

It is seen that for both properties, the curve shows a very well-defined maximum which, however, does not correspond to the hemihydrate or to equimolecular proportions of the two constituents. The position of the maximum varies with temperature; it is at about 77 per cent. at 70°, 78.5 per cent. at 60° and 80 per cent. at 50°. It is unfortunately impossible to follow the change further, since phenol ceases to be liquid at the next working temperature, but these values suffice to indicate that the maximum corresponds to a compound of equimolecular proportions of water and phenol, and that this is partially dissociated at these temperatures. The lower the temperature, the smaller is the dissociation and the nearer is the position of the maximum to the concentration corresponding to the compound.

¹² Dunstan and Thole, *J. Chem. Soc.*, **95**, 1556, 1909.

¹³ *Z. physik. Chem.*, **69**, 203, 1909.

¹⁴ *Trans. Farad. Soc.*, **8**, 20, 1912.

This is in agreement with the suggestion already made that in solutions of water and phenol, ionisation occurs in two ways :

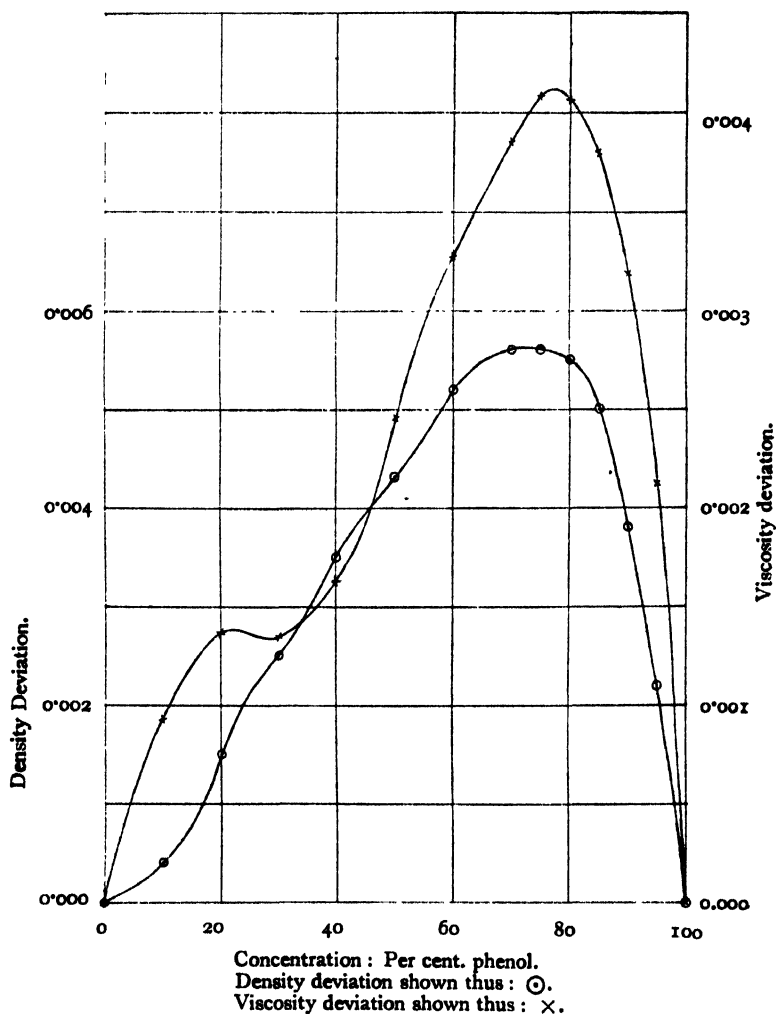
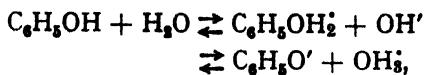


FIG. 2.

and that when the two components are present in equimolecular proportions the compound $(\text{C}_6\text{H}_5\text{OH}_2^+)(\text{OH}^-)$ is largely formed.

The curves exhibit an interesting inflexion at 20-30 per cent. phenol. It is possible that this may represent the concentration at which the first mode of ionisation begins to become appreciable. It continues to predominate up to the concentration represented by the maximum, and thereafter dissociation of the compound occurs in excess phenol.

Viscosity-Temperature Relation.

The viscosity coefficient, η , is plotted against the temperature for each concentration, in Fig. 3. It is seen that all the curves are perfectly smooth.

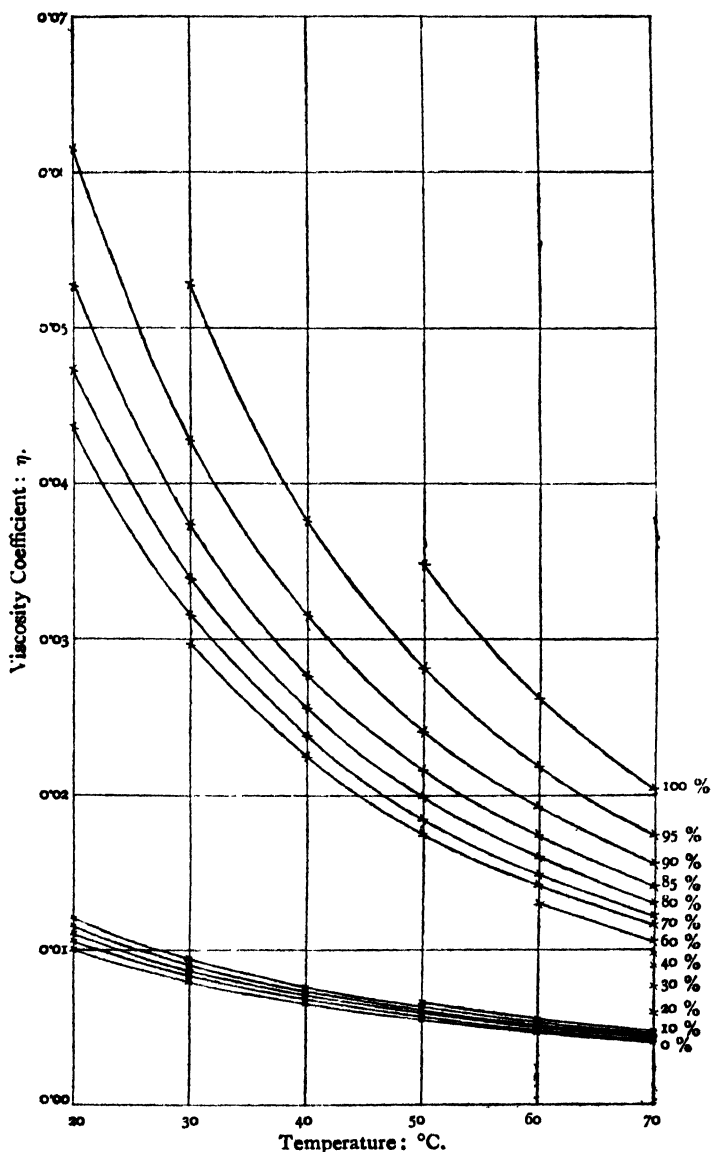


FIG. 3.

The first attempt to find a relation for the variation of the viscosity of liquids with temperatures from purely theoretical considerations, appears to be that of Sato¹⁵, who, treating the molecules as electrical

¹⁵ *Sci. Rep. Tohoku*, 14, 403, 1925.

dipoles, derived a very complicated expression which is, unhappily, far too unwieldy for general application.

Frenkel,¹⁶ basing his treatment on the heat motion of liquids, obtained the equation

$$\eta = CT e^{-\frac{U}{RT}},$$

and Dunn,¹⁷ from the temperature variation of diffusion, found a very similar relation,

$$1/\eta = Ae^{-\frac{Q}{RT}}.$$

Andrade,¹⁸ unaware of the work of these two investigators, derived from theoretical treatment which he has subsequently outlined,¹⁹ an expression identical (if $b = Q/R$) with that of Dunn in the form

$$\eta = Ae^{-\frac{b}{T}},$$

and, by a curious chance, almost simultaneously Sheppard²⁰ also gave the identical expression in the form

$$\log \phi \left(= \log \frac{1}{\eta} \right) = -\frac{K}{T} + C.$$

These equations represent the temperature variation of viscosity of "normal" (*i.e.*, unassociated) liquids with satisfactory accuracy but (as Dunn and Andrade have pointed out) they fail with associated liquids. For such liquids and for solutions, $\log \eta$ is certainly not a linear function of $1/T$.

Of the large number of empirical formulæ proposed by different observers for the variation of viscosity with temperature, the second equation of Slotte²¹ has found general acceptance. It was tested by Thorpe and Rodger²² for a large number of different liquids over a wide range of temperature, and found to be the most satisfactory. The same equation has been found to express with great accuracy the relation between viscosity and temperature for solutions, even those containing complexes,²³ over a wide range of concentration and temperature, and is now applied to the whole range of solutions in the water-phenol system.

Slotte's equation may be written

$$\eta_r = \frac{S}{(t+k)^n},$$

where S , k and n are constants. The simplest way of finding k and n is to plot $\log \eta_r$ against $\log (t+k)$ using different values of k . A few trials soon fix the value of k , which gives the straight line demanded by the Slotte equation, and the slope of this line is n .

The constant S is dependent on the other two and, since all the calculations are based on the observations at 20° , the lowest working temperature,

$$\log S = \log \eta_{20^\circ} + n \log (20 + k).$$

¹⁶ *Z. Physik*, **35**, 664, 1926.

¹⁷ *Nature*, **125**, 309, 1930.

¹⁸ *Beibl.*, **16**, 182, 1892.

²³ Howell, *J. Chem. Soc.*, 162, 1929.

¹⁹ *Trans. Farad. Soc.*, **22**, 401, 1926.

²⁰ *Ibid.*, 582.

²¹ *Ibid.*, 489.

²² *Phil. Trans., A.*, **185**, 397, 1894.

For the phenol-rich solutions, k is accepted to the nearest unit, but since the concentrations of the water-rich solutions examined are much more closely spaced, an unduly abrupt change in k , and consequently in n , is avoided by accepting the nearest integral values for 0 per cent. and 8 per cent., viz., 41 and 40, respectively, and using proportionate values for the other solutions.

The values of S , k and n for each concentration are given in Table III. and plotted in Fig. 4.

TABLE III.

Water-rich Solutions.				Phenol-rich Solutions.			
Conc. Per Cent.	S .	k .	n .	Conc. Per Cent.	S .	k .	n .
0	4.971	41	1.509	70	357.7	44	2.183
2	5.918	40.75	1.541	75	250.0	40	2.113
4	6.828	40.5	1.566	80	190.5	37	2.053
6	7.720	40.25	1.586	85	165.2	34	2.018
8	8.573	40	1.602	90	200.2	32	2.047
10	9.200	39.75	1.610	95	400.7	30	2.182
				100	1137	28	2.385

Since there is no apparent continuity in the viscosity-concentration curves between the portions for the water-rich and phenol-rich solutions, it is not surprising to find that the corresponding portions of the curves for each of the Slotte constants also have no obvious connection with one another. It will be recalled that the curves of the density constants similarly each consist of two isolated portions.

The most striking characteristic of the curves, however, is that they exhibit marked inflexions, in spite of the fact that both the viscosity-temperature and the viscosity-concentration curves are perfectly smooth over the whole phenol-rich range. The k curve shows an abrupt change of direction, and both the n and S curves show well-defined minima at a concentration corresponding to equimolecular proportions of water and phenol (83.93 per cent. phenol). It has already been shown in the previous communication that the density constants also exhibit inflexion at exactly the same point.

The existence of an association of water and phenol in equimolecular proportions, therefore, seems to be definitely indicated, and further evidence of its existence and constitution will be given in subsequent communications.

It is interesting to note that none of the viscosity relations shows any evidence of the existence of phenol hemihydrate in solution.

Fluidity.

Thorpe and Rodger²² in applying the Slotte equation to many of their observations used the expanded form

$$\eta_t = \frac{C}{1 + \alpha t + \beta t^2}$$

an expression identical with that previously employed by Poiseuille²⁴ in his original investigations.

²⁴ *Mém. Savants Etrangers*, 9, 433, 1846.

The equation may be written in the form

$$\phi_i = \phi_0(1 + \alpha t + \beta t^2)$$

where ϕ = fluidity.

This equation has been applied to all the present measurements and reproduces them very well, but not as satisfactorily as does the Slotte equation itself. The constants α and β when plotted against

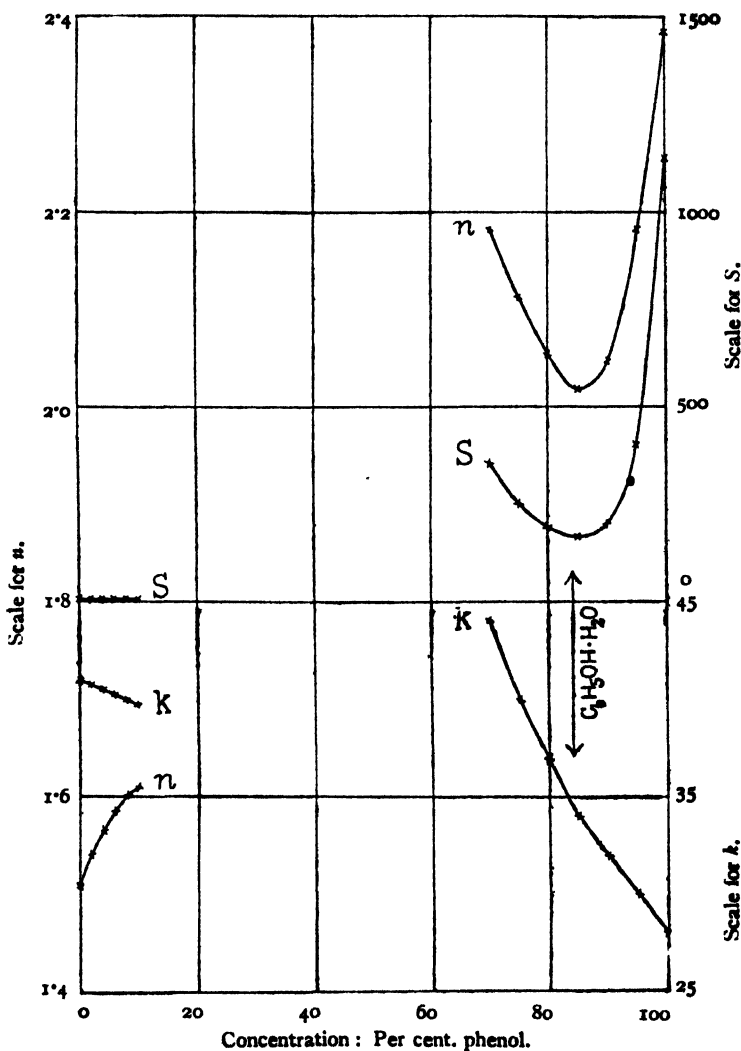


FIG. 4.

the concentration give similar curves to those obtained from the Slotte constants; the α curve shows no marked inflexion but the β curve has a well-defined minimum near the concentration corresponding to equimolecular proportions of water and phenol.

Bingham²⁵ has suggested a number of equations connecting fluidity

²⁵ *Amer. Chem. J.*, **35**, 195, 1906; **40**, 277, 1908; **43**, 287, 1910.

and temperature, one containing as many as four constants. They were found to represent the observed values with no greater accuracy than the Slotte equation and are more difficult to apply.

Relation between Temperatures of Equal Viscosity.

An interesting relation between the viscosities of pairs of different liquids at different temperatures was discovered by Porter.²⁶ If $T_1, T_2, T_3 \dots$ be the temperatures at which the viscosities of one liquid are the same as those of the other liquid at $T'_1, T'_2, T'_3 \dots$ respectively, then the ratios $T_1/T'_1, T_2/T'_2, T_3/T'_3 \dots$ are a linear function of T .

The relation does not appear to have been applied heretofore to solutions or mixtures of liquids, but a particularly interesting modification is now found for the "homologous" series of water-phenol solutions.

The range of viscosities of the water-rich solutions is too small to permit accurate readings of the temperatures of equal viscosity to be taken from the curves, but the data for the phenol-rich solutions are given in Table IV. Seven different viscosities, $\eta = 0.015, 0.020$ to 0.045 , have been chosen and the temperatures (absolute) T_e , read from the viscosity-temperature curves (Fig. 3) at which each of the solutions, 70, 75 to 100 per cent. phenol, have each of these viscosity values, are tabulated. Using the 75 per cent. solution as standard (since the 70 per cent. solution does not exist over the whole range) the ratio T_e/T_{75} is given. It is seen that, taking any pair of solutions, the ratio is practically the same for each viscosity. The Porter relation holds as for pairs of different liquids but the slope of the line is zero.

TABLE IV.

Conc. C.	$\eta = 0.015.$		$\eta = 0.02.$		$\eta = 0.025.$		$\eta = 0.03.$		$\eta = 0.035.$		$\eta = 0.04.$		$\eta = 0.045.$	
	T_e	T_e/T_{75}	T_e	T_e/T_{75}	T_e	T_e/T_{75}	T_e	T_e/T_{75}	T_e	T_e/T_{75}	T_e	T_e/T_{75}	T_e	T_e/T_{75}
70	330.4	0.993	318.0	0.994	309.2	0.994	302.5	0.993						
75	332.8	1.000	319.8	1.000	311.2	1.000	304.7	1.000	299.6	1.000	295.3	1.000	(291.7)	1.000
80	335.8	1.009	322.5	1.009	313.7	1.008	307.3	1.009	302.1	1.009	297.7	1.009	294.4	1.009
85	339.4	1.020	325.5	1.018	317.3	1.020	310.5	1.019	305.1	1.019	300.8	1.019	297.3	1.019
90	(344.1)	1.034	331.1	1.035	321.7	1.034	315.0	1.034	309.5	1.033	305.2	1.034	301.5	1.034
95			336.7	1.053	327.3	1.052	320.7	1.052	315.6	1.053	311.0	1.053	307.5	1.054
100			(343.7)	1.075	334.7	1.075	328.0	1.076	322.8	1.077	318.3	1.078		

²⁶ *Phil. Mag.*, 23, 458, 1912.

This is clearly seen from Fig. 5 where the ratio T_0/T_{75} is plotted against T_0 , a series of horizontal lines being obtained for the different concentrations.

If the ratio T_0/T_{75} be plotted against the concentration, the curve obtained is approximately parabolic. The equation

$$T_0/T_{75} = 1.000 + 1.35 \times 10^{-3}C + 6.5 \times 10^{-5}C^2$$

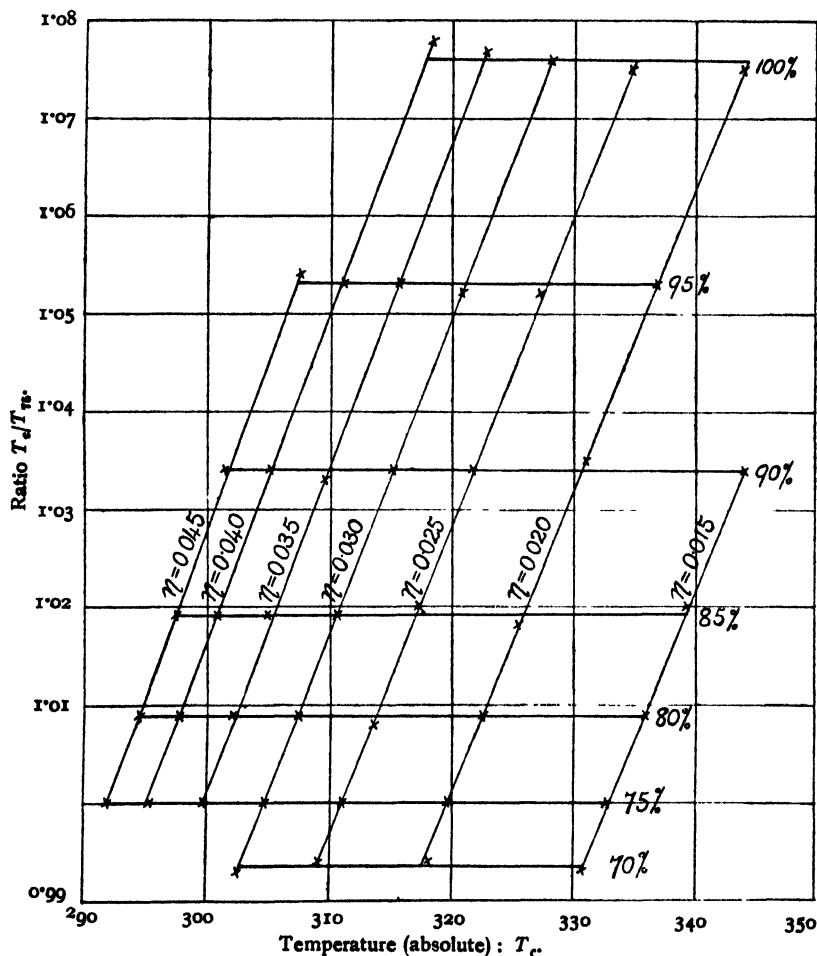


FIG. 5.

represents it with fair accuracy, the observed and calculated values being:—

Conc.	70	75	80	85	90	95	100
T_0/T_{75} obs.	0.994	1.000	1.009	1.019	1.034	1.053	1.075
„ calc.	0.995	1.000	1.008	1.020	1.035	1.053	1.074

Relative Viscosity.

The viscosity of solutions of non-electrolytes decreases with rise of temperature more rapidly than that of the solvent, so that the

relative viscosity $\frac{\eta_{\text{solution}}}{\eta_{\text{solvent}}}$ decreases with increasing temperature.

The converse is found with solutions of electrolytes.²⁷

The relative viscosities at different temperatures of three representative solutions in the water-phenol system are given in Table V.

TABLE V.

Temp. °C.	$\frac{\eta_{\text{solution}}}{\eta_{\text{water}}}$			$\frac{\eta_{\text{solution}}}{\eta_{\text{phenol}}}$
	4 Per Cent.	75 Per Cent.	90 Per Cent.	90 Per Cent.
20	1.100	4.346	6.110	—
30	1.088	3.942	5.362	—
40	1.080	3.632	4.817	—
50	1.072	3.378	4.399	0.6932
60	1.064	3.160	4.062	0.7307
70	1.058	2.982	3.799	0.7628

The 4 per cent. solution is one of phenol in water. Phenol, though not a good electrolyte, is certainly slightly dissociated and the solution is a fair conductor. The relative viscosity decreases with rise of temperature as for a non-electrolyte, but the decrease is very small over so wide a range.

The 75 per cent. solution is one of the compound $(\text{C}_6\text{H}_5\text{OH}_2)(\text{OH})$ in water. The compound is probably only slightly dissociated at this dilution and, as will be shown later, the solution is a poor conductor. The relative viscosity decreases much more rapidly than with the 4 per cent. solution.

The 90 per cent. solution, regarded as one of phenol in water, should behave as a poor electrolyte, and the relative viscosity is seen to decrease still more rapidly with rise of temperature. Actually, at this concentration, the solvent is phenol, and formation of the compound $(\text{C}_6\text{H}_5\text{OH}_2)(\text{OH})$ is proceeding by addition of water. Regarding phenol as solvent, the relative viscosity is seen to increase fairly rapidly with rise of temperature, yet the solution is an extremely poor conductor.

The application of the test of change of relative viscosity with temperature, therefore, gives no clue to the varying conditions existing in this system, and leads to some anomalous conclusions.

Relation Between Viscosity and Specific Volume.

The first suggestion of a relation between viscosity and specific volume was apparently that of Batschinski,²⁸ who gave the empirical formula

$$\eta = \frac{c}{v - w},$$

whence

$$\phi = \frac{v - w}{c},$$

where v is the specific volume and w and c are constants.

²⁷ Taylor and Ranken, *Trans. Roy. Soc. Edin.*, **45**, 397, 1906.

²⁸ *Z. physik. Chem.*, **84**, 643, 1913.

The term w is evidently the specific volume at zero fluidity and is, therefore, the "limiting volume." $v - w$ is, therefore, the "free volume."

Batschinski applied his formula to a large number of liquids, using the data of Thorpe and Rodger, and found that it held for nearly all normal liquids. With associated liquids, however, the plot of ϕ against v gives a curve concave to the ϕ axis.

TABLE VI.—80 PER CENT. PHENOL.

t	ϕ	v	$\frac{\phi_t - \phi_{80}}{v_t - v_{80}} \times 10^{-3}$
20	21.14	0.9455	1.000
30	29.47	0.9527	1.157
40	39.17	0.9603	1.218
50	50.48	0.9680	1.304
60	62.84	0.9758	1.376
70	77.01	0.9842	1.444

water-phenol solutions. The fluidity-specific volume curve is concave to the axis of fluidity as for all associated liquids, and the extent of the deviation from a straight line is indicated in the last column of the table.

The fundamental similarity of Batschinski's expression to the Slotte equation is not immediately evident, and does not appear to have been pointed out.

$$\begin{aligned}
 \phi &= \frac{v - w}{c} \\
 &= \frac{v_0(1 + \alpha t + \beta t^2) - w}{c} \\
 &= \frac{1 + \alpha t + \beta t^2 - w/v_0}{c/v_0} \\
 &= \frac{1 + \alpha t + \beta t^2 - w''}{c''}
 \end{aligned}$$

But from the expanded form of the Slotte equation,

$$\phi = \frac{1 + \alpha' t + \beta' t^2}{c'}$$

Hence Batschinski's equation is only a modified form of the Slotte equation, and will, therefore, hold only when the relative values of the coefficients of expansion of the liquid are comparable with those for the increase of viscosity.

Relation Between Viscosity and Free Space.

A very successful attempt to correlate expansion and viscosity is that of McLeod,²⁹ who has given the equation

$$\eta_t(x_t)^A = \text{const.}$$

where x_t is the free space at t° , and A is a constant. Assuming the expansion of a liquid to be that of the free space only, then

$$x_t = x_0 + \alpha t + \beta t^2 + \gamma t^3$$

²⁹ *Trans. Farad. Soc.*, 19, 6, 1923; 21 151, 1925.

where x_0 is the free space at 0° , and α , β and γ are the coefficients of expansion, and the equation becomes

$$\frac{\eta_0}{\eta_t} = \left(\frac{x_0 + \alpha t + \beta t^2 + \gamma t^3}{x_0} \right)^A.$$

McLeod has tested this equation for a large number of liquids using the data of Thorpe and Rodger for the viscosities and coefficients of expansion, and has shown that it reproduces the observed values of the viscosity very satisfactorily. McLeod claims that the equation gives better agreement with fewer constants than the Slotte equation, but he overlooks the fact that Thorpe and Rodger used the expanded form which, as we have found, does not give the accuracy of the original.

It does not appear to have been pointed out that McLeod's equation is an extended form of the Slotte equation. Simplifying the right-hand side, McLeod's equation may be written

$$\begin{aligned} \frac{\eta_0}{\eta_t} &= \left(1 + \frac{\alpha}{x_0}t + \frac{\beta}{x_0}t^2 + \frac{\gamma}{x_0}t^3 \right)^A \\ &= (1 + \alpha't + \beta't^2 + \gamma't^3)^A \end{aligned}$$

and Slotte's equation may be written

$$\begin{aligned} \frac{\eta_0}{\eta_t} &= \left(\frac{k+t}{k} \right)^n \\ &= (1 + t/k)^n \\ &= (1 + \alpha''t)^n. \end{aligned}$$

It is, therefore, seen that McLeod's equation is of the same form as Slotte's, but contains two more constants with second and third power terms of the temperature, so that if these constants were arbitrary, the equation should give better agreement than the Slotte equation. The value of McLeod's equation, however, lies in the fact that definite significance is attached to the constants α , β and γ .

The equation has apparently not hitherto been applied to solutions, but is now found to give excellent agreement for water-phenol mixtures. The values for 80 per cent. phenol only are quoted, but are typical.

Since measurements were not made below 20° , x_{20° is taken instead of x_0 in the equation. The value of x_{20° and of A have been calculated for different combinations of the observed viscosities and are given in Table VII.

TABLE VII.

Range.	x_{20° .	Range.	A .
20 30 50	0.03425	20 30	1.665
20 40 60	0.03670	20 40	1.649
20 50 70	0.03250	20 50	1.663
Mean	0.03448	20 60	1.659
		20 70	1.655
		Mean	1.658

The viscosities calculated using the mean values are given in Table VIII. and the agreement with the observed values is seen to be

very good. The second column in Table VIII contains the values of $\alpha t + \beta t^2 + \gamma t^3 + \dots$ obtained from the density measurements given in the previous communication.

TABLE VIII.

80 per cent. phenol.

 $\kappa_{20^\circ} = 0.03448$. $A = 1.658$.

t .	Expansion.	η_s° (obs.).	η_s° (calc.).	Difference Per Cent.
20	0	0.04731	0.04731	0.00
30	0.00762	0.03393	0.03398	+ 0.15
40	0.01565	0.02553	0.02545	- 0.08
50	0.02371	0.01981	0.01986	+ 0.25
60	0.03201	0.01591	0.01593	+ 0.13
70	0.04084	0.01298	0.01295	- 0.23

It may be noted that the free space for this solution is very small, almost the same at 20° as for propyl alcohol at 0° , indicating that the association is great. The value of A , which is only about unity for unassociated liquids, is high as with all associated liquids.

Line of Mean Viscosity.

The viscosity coefficients of the conjugate solutions at each temperature, and their means, are given in Table IX. and plotted in Fig. 6.

TABLE IX.

Temp. °C.	Viscosity Coefficient η .			
	Water Layer.	Phenol Layer.	Mean (obs.).	Mean (calc.).
20	0.01220	0.04199	0.02710	0.02710
30	0.009622	0.02949	0.01956	0.01958
40	0.008014	0.02178	0.01490	0.01488
50	0.006949	0.01645	0.01170	0.01173
60	0.006438	0.01258	0.00951	0.00951
62	0.006494	0.01186	0.00918	0.00915
64	0.006752	0.01115	0.00895	(0.00880)
66	0.007365	0.01038	0.00887	(0.00847)

The curves for both the conjugate solutions and the means are much more markedly curved than the corresponding density curves, and they are convex to the axis of the temperature, whereas those for the density are concave. As with the densities of the conjugate solutions, the top of the curve is very flat and the mean line is quite smooth.

No equation to the line of mean viscosity appears to have been suggested previously, but it is now found that the Slotte equation

$$\eta_s^\circ = \frac{s}{(t + k)^n}$$

holds very accurately over the whole range, except in the immediate neighbourhood of the critical solution temperature.

The values calculated from this equation with

$$\begin{aligned}s &= 28.88 \\ k &= 30 \\ n &= 1.782\end{aligned}$$

are given in Table IX., where the agreement with the observed values is seen to be very good up to 62°.

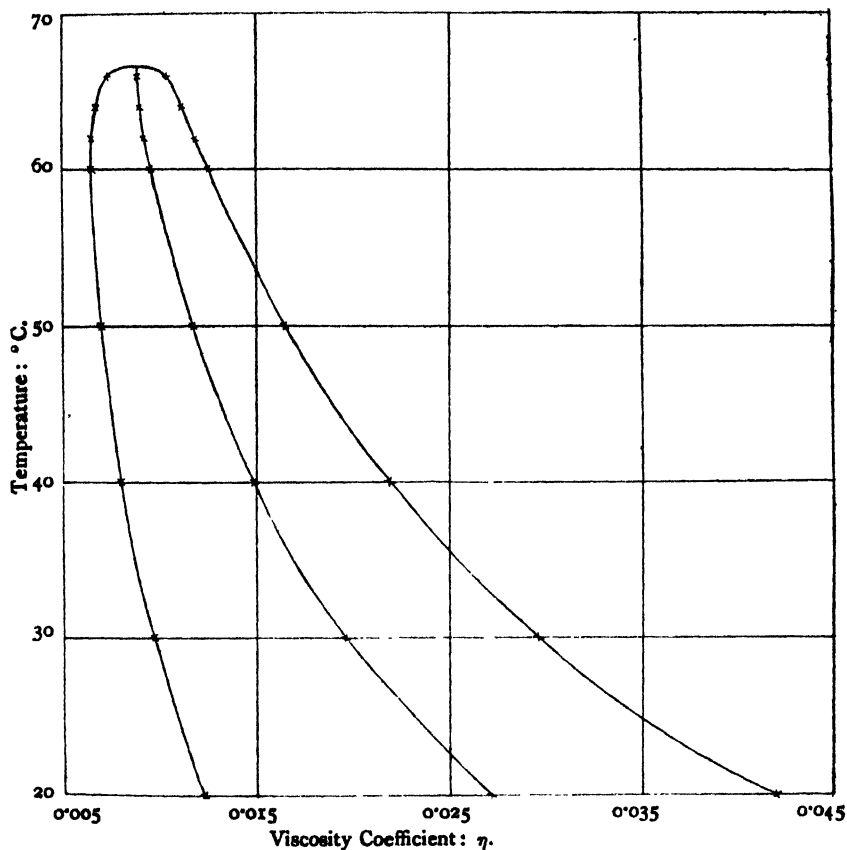


FIG. 6.

It follows from the expanded form of the Slotte equation that an equation of the type

$$\phi_t = \phi_{20} (1 + \alpha\theta + \beta\theta^2)$$

where
and

$$\begin{aligned}\phi &= \text{fluidity} \\ \theta &= t - 20\end{aligned}$$

fits the curve almost equally well, so that there is an exactly similar relation for the line of mean fluidity as for the line of mean density.

It is seen from the curve that the viscosity coefficient of the critical solution is approximately 0.00885.

Summary.

1. The viscosity coefficients of a series of solutions of water and phenol of different concentrations, suitably spaced over the whole range of miscibility, have been measured at 20°, 30°, 40°, 50°, 60° and 70°.

2. The viscosity-concentration curve for each temperature is complex and, as with the densities, there is no simple continuity between the portion for the water-rich and that for the phenol-rich solutions.

3. The curve of the deviation of viscosity from the ideal mixture law (assumed linear) against concentration indicates combination between water and phenol in equi-molecular proportions. It has been previously suggested that this results from ionisation occurring in two ways.

4. The viscosity-temperature curve for each concentration is smooth and is accurately represented by the Slotte equation,

$$\eta^s = \frac{S}{(t + k)^n},$$

the constants S , k and n having different values for the different concentrations.

5. The curves of the constants S and n plotted against the concentration exhibit sharp minima, and that of k an inflexion, all at approximately 84 per cent. phenol, corresponding to equimolecular proportions of water and phenol, thus confirming the similar observations found with the density-temperature constants and the suggestion of compound formation.

6. Fluidities have been calculated from the expanded form of the Slotte equation and, for these also, the constants plotted against concentration exhibit inflexion near the concentration corresponding to equi-molecular proportions of water and phenol.

7. An interesting relation, which is an extension of the Porter relation for pairs of different liquids, has been discovered between temperatures of equal viscosity for an "homologous" series of solutions.

8. The application of the rule, that relative viscosity of solutions of non-electrolytes decreases and of electrolytes increases with rise of temperature, to solutions of different concentrations of water and phenol leads to some anomalous conclusions.

9. Batschinski's relation between viscosity and specific volume has been applied to solutions of water and phenol. The fluidity-specific volume curve is concave to the axis of fluidity as for associated liquids.

10. McLeod's equation for the relation between viscosity and free space has been applied to solutions in this system and found to give excellent agreement with the observed values. It is shown that both Batschinski's and McLeod's equations are expanded forms of the Slotte equation.

11. The line of mean viscosity is accurately represented by the Slotte equation

$$\eta^{\text{mean}} = \frac{28.88}{(t + 30)^{1.758}}$$

over the whole range, except very near the critical solution temperature.

12. The critical solution viscosity is 0.00885.

*The College of Technology,
Manchester.*

ERRATA.

Page 321—below formula 2—for T and T' , read I and I' .

Page 325—11 lines from bottom—for c/v^3 , read c/v^2 .

Page 328—add footnote: The measurements given in Fig. 9 are due to A. S. Coolidge, *J. Am. Chem. Soc.*, **48**, 1795 (1926).

Page 358—the numbers on the left side of Fig. 14 should read: -1 , -1 , 0 , $+20$, $+40$, $+60$, $+80$. 10 lines from the bottom to read: To twice the energy values of these surfaces, we add the dissociation energy.

Transactions of the Faraday Society.

INDEX—VOLUME XXVIII., 1932.

	PAGE
Allmand, A. J., Burrage, L. J., and Chaplin, R. Discontinuities in Adsorption Processes	218
— — — — — and Chaplin, R. A Possible Connection between Activated Adsorption and Gas Displacement Effects	223
Barak, M., and Taylor, H. S. The Photochemical, Mercury-Sensitised Reactions between Hydrogen, Oxygen and Carbon Monoxide	569
Bawn, C. E. H. See <i>Lochte-Holtgreven, W.</i> , and	
Becker, J. A. The use of Thermionics in the Study of Adsorption of Vapours and Gases.	148
Benton, A. F. Adsorption and Solution of Gases by Metals	202
Beebe, R. A. The Heats of Adsorption of Hydrogen and Carbon Monoxide on Copper	761
Bennett, W. H. The Behaviour of the Hydrogen Electrode in Chromic-Chromous Solutions and the Solubility Product of Chromous Hydroxide	889
Bonhoeffer, K. F., and Farkas, A. On Adsorption and Reflection Processes in the Interaction of Hydrogen and Metals	242
— — — — — Correction to the Note on Adsorption and Reflection Processes in the Interaction of Hydrogen and Metals	561
Bonnell, D. G. R. Studies in Gels. I.: Syneresis of Silica Gel.	1
— — — — — Studies in Gels. II.: Effect of Hydrogen-Ion Concentration on the Syneresis of Silica Gels	12
— — — — — Studies in Gels. III.: Vapour Pressure of Silica Gels	463
Borgmann, C. W. See <i>Evans, U. R.</i> , and	
Bosworth, R. C. Studies in Adsorption. Part I.: Adsorption of Carbon Dioxide, Sulphur Dioxide and Water	896
— — — — — Studies in Adsorption. Part II.: Adsorption of the Lower Fatty Acids	903
Bragg, W. L., and Darbyshire, J. A. The Structure of Thin Films of Certain Metallic Oxides	522
Britton, H. T. S. and Westcott, O. B. The Electrodeposition of Chromium from Tervalent Chromium Salt Solutions. Part II.: Chromium Acetate, Oxalate and Tartrate Baths	627
— — — — — and Robinson, R. A. The use of the Glass-Electrode in Titrimetric Work and Precipitation Reactions. The Application of the Principle of the Solubility Product to Basic Precipitates	531
Bungenberg de Jong, H. L., and Klaar, W. J. Colloid Chemistry of Gliadin. Separation Phenomena	27
— — — — — Colloid Chemistry of Gluten. (Binary Protein Mixtures)	798
Burdon, R. S. The Surface Tension of Mercury in a Silica Apparatus	866
Burstein, R., and Frumkin, A. The Sorption of Hydrogen by Platinised Charcoal	273
Burrage, L. J. Criticism of Some Experimental Evidence for Activated Adsorption	192
— — — — — Investigation of the System $KCl - PbCl_2 - H_2O$ at $25^\circ C$	529
— — — — — See <i>Allmand, A. J., Chaplin, R.</i> , and	
Burt, F. P. Sorption of Gases by Glass	179
Butler, J. A. V. The Mechanism of Overvoltage and its Relation to the Combination of Hydrogen Atoms at Metal Electrodes	379
Campbell, A. N., and Yanick, N. S. The System $NiSO_4 - CaSO_4 - H_2O$	657
Campbell, A. N. See <i>Carter, H. D.</i> , and	
Campbell, C., King, A. and Whitworth, C. The Propagation of Explosion Waves through a System of Glass and Rubber Tubes	681
Carter, H. D., and Campbell, A. N. Electric Discharges in Liquids. Part I.: The Arc Discharge in Water	479
— — — — — Electric Discharges in Liquids. Part II.: The Arc Discharge in Water (<i>continued</i>)	634
Cassel, H. The Thickness of Adsorbed Films on Mercury	177

Chaplin, R. See <i>Allmand, A. J.</i> , and — See <i>Allmand, A. J.</i> , <i>Burrage, L. J.</i> , and	
Chariton, J., <i>Schalnikoff, A.</i> , and <i>Semenoff, N.</i> On the Behaviour of Adsorbed Atoms	169
Constable, F. H., and <i>Ward, A. F. H.</i> Catalysis and Photo-Conductors	497
— The Kinetics of Adsorption in Relation to Reaction Velocity	227
Darbyshire, J. A. See <i>Bragg, W. L.</i> , and	
Davies, C. W. The Determination of the Mobilities of Anions of Weak Acids	607
— See <i>Money, R. W.</i> , and	
Desai, B. N., and <i>Nabar, G. M.</i> The Influence of Hydrolysed Gelatin on the Precipitation of Silver Chromate	449
Dohse, H., and <i>Mark, H.</i> On Mixture Isotherms at Active Points.	165
Egerton, A. See <i>Ubbelohde, A. R.</i> , and	
Ellis, O. C. de C., and <i>Morgan, E.</i> The "Vibratory Movement" in Flames.	826
Emeleus, H. J. The Photochemical Reaction of Carbon Monoxide with Ammonia and with Amines	89
Evans, M. G. Deviations from the "Ideal" Translation Motion of Adsorbed Molecules	364
— Unimolecular Reaction Velocity	840
Evans, U. R., and <i>Borgmann, C. W.</i> The effect of Oxygen Pressure on the Corrosion of Steel	813
Farkas, A. See <i>Bonhoeffer, K. F.</i> , and	
Foster, A. G. The Sorption of Condensable Vapours by Porous Solids. Part I.: Applicability of the Capillary Theory.	645
Fowler, R. H. Theories of Adsorption of Gases. Quantum Mechanics of the Reversible Electrolytic Cell and of Electrolysis	368
Frankenburger, W., and <i>Hodler, A.</i> New Experiments on the Mechanism of the Catalysis of Ammonia on Tungsten	229
Freundlich, H. Introductory Paper to Section II. of General Discussion on Adsorption of Gases by Solids: Kinetics and Energetics of Gas Adsorption	195
Frumkin, A. See <i>Burstein, R.</i> , and	
Garner, W. E. The Heats of Adsorption and the Kinetics of Adsorption	261
Glasstone, S., and <i>Speakman, J. C.</i> The Electrodeposition of Iron-Cobalt Alloys. Part I.	733
— and <i>Reynolds, G. D.</i> The influence of High Frequency Currents on Polarised Electrodes. Part I.	582
Griffith, R. O., <i>McKeown, A.</i> , and <i>Winn, A. G.</i> The Bromine-Bromine-Tribromide Equilibrium	101
— — — The Kinetics of the Bromine-Oxalate Reaction	107
— — — The Kinetics of the Oxidation of Oxalic Acid by Chlorine	518
— — — The Kinetics of the Iodine-Oxalate Reaction	752
Hassid, N. J. See <i>Maxted, E. B.</i> , and	
Hinshelwood, C. N. The Role of Surface Adsorption in Chain Reactions	184
Hodler, A. See <i>Frankenburger, W.</i> , and	
Howell, O. R. A Study of the System Water-Phenol. Part II.: Viscosities	912
Howitt, F. O. See <i>Prideaux, E. B. R.</i> , and	
Hückel, E. Theory of Heat Evolved in Capillary Condensation	382
Inglis, N. P., and <i>Lake, G. F.</i> Corrosion-Fatigue Tests of Nitrided Steel and Nickel-Plated Steel in River Tees Water	715
Jeffery, F. H. Thermodynamics applied to the Iron-Carbon System	98
— The α and β Solid Solutions of the Copper-Zinc Alloys and the Corresponding Liquid Solutions in Equilibrium with them Examined Thermodynamically	452
— The Constitution of the Liquid and Solid Alloys of the Copper-Gold System Examined Thermodynamically	455
— The Lead Rich Alloys of the System Lead-Antimony Examined Thermodynamically	567
— The Constitution of the Copper-Silver Series of Alloys Examined, Thermodynamically	705

	PAGE
Johnson, C. H. Studies in Optical Activity. Part I.: A Contribution to Valence Theory	845
Johnson, M. C. Pressure Measurements for Investigating the Mutual Behaviour of Adsorbed Hydrogen Atoms	162
Jowett, M., and Price, H. I. Solubilities of the Phosphates of Lead	668
King, A. See <i>Campbell, C., Whitworth, C., and</i>	
Kingman, F. E. T. The Adsorption of Hydrogen by Charcoal	269
Klaar, W. J. See <i>Bungenberg de Jong, H. L., and</i>	
Lake, G. E. See <i>Inglis, N. P., and</i>	
Laybourn, K., and Madgin, W. M. On the Measurement of Mechanical Properties of Binary Inorganic Salt Mixtures	857
Lee, A. R. The Effect of Oxygen Pressure on the Corrosion of Steel	707, 813, 825
Lennard-Jones, J. E. Processes of Adsorption and Diffusion on Solid Surfaces	333
Lewis, W. C. M. Note on the Electric Charge on an Oil Droplet in an Emulsion	597
Liu, C. L. See <i>Yap Chu Phay, and</i>	
Lochte-Holtgreven, W., and Bawn, C. E. H. The Heat of Formation and Structure of the Carbon-Oxygen and Carbon-Sulphur Linkages	698
Madgin, W. M. See <i>Laybourn, K., and</i>	
Magnus, A. The Electrical Theory of Gaseous Adsorption	386
Mardles, E. W. J. The Oxidation of Fuel Vapours in Air—Discussion	69
Mark, H. See <i>Dohse, H., and</i>	
Maxted, E. B., and Hassid, N. J. The Kinetics of the Adsorption of Hydrogen on Platinum and Nickel	253
McBain, J. W. Persorption and Monomolecular Sieves	408
McKay, A. T. Absorption and Classical Diffusion	721
McKeown, A. See <i>Griffith, R. O., Winn, A. G., and</i>	
— See <i>Griffith, R. O., and</i>	
Melville, H. W. The Inhibition of the Photochemical Decomposition of Ammonia by Atomic Hydrogen	885
— The Oxidation of Phosphorous Vapour at Low Pressures	308
— Inert Gas Effects in Chain Reactions	814
Money, R. W., and Davies, C. W. The Extent of Dissociation of Salts in Water. Part IV.: Bi-bivalent Salts	609
Moorhouse, G. B. The Electrolysis of Fused Acetates and Propionates	766
Morgan, E. See <i>Ellis, O. C. de C., and</i>	
Morris, G. See <i>Taylor, W., and</i>	
Morton, C. Glass Electrode Studies. Some Cupric Hydroxy-Acid Complexes	84
Müller, W. J. The Time Factor in Anodic Passivation of Metals. Remarks on the paper of Shutt and Stirrup	471
Nabar, G. M. See <i>Desai, B. N., and</i>	
Neale, S. M., and Stringfellow, W. R. The Solubility of Barium Hydroxide in Dilute Solutions of Sodium Hydroxide	765
Norris, M. H. The Swelling of Wool Fibres in Water and in Aqueous Solutions of Sodium Hydroxide, as shown by the Change in Cross-Sectional Area	618
Paul, B. See <i>West, W., and</i>	
Perlitz, H. On Variations of Inter-Atomic Distances with the Change from the Cubic Face-centered Arrangement to the Cubic Body-centered or to the Hexagonal Close-packed Arrangement	514
Polanyi, M. Introductory Paper to Section III. of General Discussion on Adsorption of Gases by Solids: Theories of Adsorption of Gases. A General Survey and Some Additional Remarks	316
Porter, A. W. The Vapour Pressures of Binary Mixtures	95
Price, H. I. See <i>Jowett, M., and</i>	
Prideaux, E. B. R., and Howitt, F. O. The Electrophoresis of Agar-Gold Sols	79
Reynolds, G. D. See <i>Glasstone, S., and</i>	
Rideal, E. K. Introductory Paper to Section I. of General Discussion on Adsorption of Gases by Solids: Experimental Methods	139

	PAGE
Roberts, J. K. The Interchange of Energy in Collisions between Gas Atoms and Solid Surfaces	395
Robinson, R. A. See <i>Britton, H. T. S.</i> , and	
Schalnikoff, A. See <i>Chariton, J.</i> , <i>Semenoff, N.</i> , and	
Schuster, C. Hydrogenation of Adsorbed Ethylenic Hydrocarbons	406
Semenoff, N. See <i>Chariton, J.</i> , <i>Schalnikoff, A.</i> , and	
Semenov, N. N. Some General Considerations in Connection with the Chain-Reaction Theory	818
Sherman, A. See <i>Taylor, H. S.</i> , and	
Shukla, S. N. , and Walker, O. J. Anode Phenomena in the Electrolysis of Potassium Acetate. Part III.: Formation of Methane	457
Shutt, W. J. , and Walton, A. The Passivity of Gold	740
Speakman, J. C. See <i>Glasstone, S.</i> , and	
Steacie, E. W. R. Solubility and Activated Adsorption	617
Stringfellow, W. R. See <i>Neale, S. M.</i> , and	
Sumner, C. G. An Improved Sedimentation Method for the Determination of Particle Sizes, using an Automatic Recorder	20
Taylor, H. S. General Introduction to the General Discussion on The Adsorption of Gases by Solids	131
Taylor, H. S. , and Sherman, A. Activated Adsorption of Hydrogen and the Para-Hydrogen Conversion	247
Taylor, H. S. See <i>Barak, M.</i> , and	
Taylor, W. , and Morris, G. The Absolute Measurement of the Available Energy of High Explosives by the Ballistic Mortar	545
Thompson, H. W. The Explosive Combination of Hydrogen and Oxygen. The Function of Walls in Gaseous Reactions	299
Trew, V. C. G. Physical Properties of Mixtures of Acetone and Bromoform	509
Tryhorn, F. G. , and Wyatt, W. F. Adsorption of Saturated Vapours by Porous Substances. Experimental Methods	158
Ubbelohde, A. R. The Kinetics of Adsorption Processes. II.: The Occlusion of Hydrogen by Palladium. Part I.: Discussion.	275
— The Kinetics of Adsorption Processes. III.: The Influence of Nuclear Spin on the Sorption of Hydrogen on Charcoal	291
— and Egerton, A. The Kinetics of Adsorption Processes: The Occlusion of Hydrogen by Palladium. Part II.: Dynamic Isothermals	284
Volmer, M. The Migration of Adsorbed Molecules on Surfaces of Solids	359
Walker, O. J. See <i>Shukla, N.</i> , and	
Walton, A. See <i>Shutt, W. J.</i> , and	
Ward, A. F. H. See <i>Constable, F. H.</i> , and	
— The Suggested Existence of Activated Adsorption	399
Wellings, A. W. The Direct Titration of Magnesium and Manganous Sulphates, using Fluorescein as an Adsorption Indicator, and the Extension of the Method to the Direct Titration of Other Soluble Sulphates and Alums	561
— The Direct Titration of Normal Oxalates in Neutral Solution, using Fluorescein as an Adsorption Indicator	565
— The Direct Titration of Nitrates with Titanous Chloride, using Alizarin as an Adsorption Indicator	665
West, W. , and Paul, B. The Quantum Yield in the Photo-decomposition of the Alkyl Halides in Non-Polar Solvents	688
Westcott, O. C. See <i>Britton, H. T. S.</i> , and	
Whitby, L. A Method for the Measurement of the Dissolution of Metals in Salt Solutions	474
Whitworth, C. See <i>Campbell, C.</i> , <i>King, A.</i> , and	
Winn, A. G. See <i>Griffith, R. O.</i> , <i>McKeown, A.</i> , and	
Woods, H. J. The Energy of the Ground State of Methane	877
Wyatt, W. F. See <i>Tryhorn, F. G.</i> , and	
Yanick, S. See <i>Campbell, A. N.</i> , and	
Yap Chu Phay. The Free Energy of Transition of Iron ($\alpha \rightleftharpoons \gamma$)	781
— and Liu, C. L. The Free Energy, Entropy and Heat of Formation of Iron Carbide (Fe_3C)	788

Indian Agricultural Research Institute (Pusa)
LIBRARY, NEW DELHI-110012

This book can be issued on or before

Return Date	Return Date